# ELUCIDATING THE SOLID, LIQUID, AND GASEOUS PRODUCTS FROM BATCH PYROLYSIS OF COTTON-GIN TRASH

A Thesis

by

FROILAN LUDANA AQUINO

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

December 2007

Major Subject: Biological and Agricultural Engineering

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Approved by:

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| Chair of Committee, | Sergio C. Capareda |
| Committee Members, | Calvin B. Parnell, Jr. |
| | Jerald A. Caton |
| Head of Department, | Gerald L. Riskowski |

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# ABSTRACT

Elucidating the Solid, Liquid**,** and Gaseous Products from Batch Pyrolysis of Cotton-gin Trash. (December 2007)

Froilan Ludana Aquino, B.S., University of the Philippines at Los Baños, Philippines

Chair of Advisory Committee: Dr. Sergio C. Capareda

Cotton-gin trash (CGT) was pyrolyzed at different temperatures and reaction times using an externally-heated batch reactor. The average yields of output products (solid/char, liquid/bio-oil, and gaseous) were determined. The heating value (HV) of CGT was measured to be around 15-16 MJ $kg^{-1}$ (6500-7000 Btu $lb^{-1}$). In the first set of tests, CGT was pyrolyzed at 600, 700, and 800°C and at 30, 45, and 60 min reaction period. The maximum char yield of 40% by weight (wt.%) was determined at 600°C and 30 min settings, however, the HV of char was low and almost similar to the HV of CGT. A maximum gas yield of 40 wt.% was measured at 800°C and 60 min and the highest liquid yield of 30 wt.% was determined at 800°C and 30 min. In the modified pyrolysis test, the effects of temperature (500, 600, 700, and 800°C) on the product yield and other properties were investigated. The experiment was performed using the same reactor purged with nitrogen at a rate of 1000 $cm^3$ $min^{-1}$. Gas yield increased as temperature was increased while the effect was opposite on char yield. The maximum char yield of 38 wt.% was determined at 500°C and 30 min. The char had the largest fraction in the energy output (70-83%) followed by gas (10-20%) and bio-oil (7- 9%). Maximum gas

yield of 35 wt.% was determined at 800°C. The average yield of CO, $H_2$ and total hydrocarbons (THC) generally increased with increased temperature but $CO_2$ production decreased. Methane, ethane, and propane dominated the THC. The bio-oil yield at 600°C was the highest at about 30 wt.% among the temperature settings. The HV of bio-oil was low (2-5 MJ $kg^{-1}$) due to minimal non-HC compounds and high moisture content (MC). A simple energy balance of the process was performed. The process was considered energy intensive due to the high amount of energy input (6100 kJ) while generating a maximum energy output of only 10%. After disregarding the energy used for preparation and pyrolysis, the energy losses ranged from 30-46% while the energy of the output represent between 55-70% of the input energy from CGT.

# DEDICATION

*For my family…*

*(my mom and my dad who just turned 65 and recently retired from service)…*

*For my friends…*

*(who are always around to support me even in spirit)…*

*For the environment…*

*(one of God's greatest gifts for mankind)…*

*For the FUTURE!*

*(learn from the past, apply them today*

*and keep moving forward)…*

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# NOMENCLATURE

| | |
|---|---|
| CGT | Cotton-gin Trash |
| HC | Hydrocarbons |
| THC | Total hydrocarbons |
| $\sigma$ | Standard deviation |
| MC | Moisture content |
| a.r. | As-received |
| $V_G$ | Gas volume |
| GC/MS | Gas chromatograph/Mass spectrometer |
| NDIR | Non-destructive infrared |
| TCD | Thermal conductivity detector |
| FID | Flame-ionization detector |
| $C_1$ | Methane |
| $C_2$ | Ethane |
| $C_3$ | Propane |
| $C_4$ | *N*-Butane |
| $C_5$ | *N*-Pentane |
| $C_6$ | *N*-Hexane |
| ASTM | American Society of Testing and Materials |

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# 1. INTRODUCTION: THE IMPORTANCE OF RESEARCH

The world's dependence on fossil fuel as the main source of energy has continuously increased through time because of the rapid industrial and economic development and increase in population. With the inevitable depletion of fossil fuel reserves, developing renewable energy, renovating energy source structures, and keeping sustainable development safe should be focused on (Qi et al., 2006).

Biomass has received significant attention in the scientific community as a renewable source of energy since the oil crises in the early 1970s (Bridgewater and Grassi, 1991). All organic matter (i.e., plants, woods, and animal wastes) are considered biomass. Therefore, biomass can be considered unlimited and readily available. Moreover, the production of fuel from biomass would not significantly contribute to atmospheric $CO_2$ increase as compared to fossil fuels (Boateng et al., 2006). Biomass resources such as forest residues, agricultural residues, and municipal solid wastes are composed of organic raw materials that can be converted to energy (Caglar and Demirbas, 2000). In addition, biomass wastes have lower sulfur and nitrogen content that give lower $SO_2$ and $NO_x$ emissions, respectively, compared to conventional fossil fuels, thus keeping the environment and the public health safe (Qi et al., 2006; Tsai et al., 2006A).

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This thesis follows the style of the *Transactions of the American Society of Biological and Agricultural Engineers (ASABE).*

The high production of agricultural wastes could provide considerable amount of energy if properly utilized (Williams and Nugranad, 2000). With the application of thermochemical conversion processes on biomass, fuels with higher heating values (HVs) could be produced efficiently and economically, instead of just combusting the biomass directly to produce heat or power (Caglar and Demirbas, 2000).

Texas is one of the largest producers of cotton in the United States, yielding more than 1.5 million tons of cotton-gin trash (CGT) each year (NASS, USDA 2006 Annual Report). One of the main problems faced by large cotton-gin facilities in Texas is the disposal of cotton-gin trash. Currently, the cost associated with cotton-gin trash disposal is high, amounting to more than $ 2 million every year. The typical methods of CGT disposal include the following: (1) composting or mulching; (2) addition to feed roughage; and (3) land filling. Among the most commonly utilized methods for gin trash disposal, incineration could be considered the fastest but it also imposes several health hazards. The potential of cotton-gin trash for energy production is promising. Cotton-gin trash has different characteristics compared to other types of biomass commonly used in pyrolysis and, therefore, further research is needed on its composition to attain optimum energy conversion (Zabaniotou et al., 2000).

This study was designed to determine the different products (solid, liquid, and gas) from batch pyrolysis of CGT. The specific objectives are as follows:

a. To determine the effect of temperature and reaction time on the solid, liquid, and gaseous product yield from CGT;

b. To evaluate the quality of the solid, liquid, and gaseous products using proximate and heating value analysis;
c. To identify the conditions to maximize the solid (char), liquid, and gaseous products from CGT pyrolysis;
d. To perform a simple energy and mass balance on the biomass after pyrolysis.

# 2. REVIEW OF RELATED LITERATURE

## 2.1. *Pyrolysis: Overview*

Pyrolysis or destructive distillation is a direct thermal conversion process in the complete absence of an oxidant. It is the first step to thermo-chemical conversion that yields a wide variety of products such as condensable gases and tars (bio-oils), non-condensable gases (synthesis gas or syngas), and char (Boateng et al., 2006). All of these products have potential end use. Certain factors determine the amount and variety of these output products, therefore the pyrolysis conditions can be optimized for either char, gas, or oil production (Encinar et al., 1997; Williams and Nugranad, 2000).

The product yields of pyrolysis mainly depend on the reaction temperature and the heating rate. Normally, lower process temperature and longer reaction period favors the production of char and high temperatures and short residence times would favor the production of liquids (EIA, 2007). In addition, longer pyrolysis time at higher temperatures increases the production of gaseous products or syngas. There are several modes of pyrolysis available and these are as follows: (a) fast or flash pyrolysis – characterized by moderate temperatures of about $500^{o}$C with short retention times of less than 2 s, fast pyrolysis at lower temperatures usually increases the liquid product yield; (b) vacuum pyrolysis – characterized by subatmospheric pressure conditions to lower the boiling point of biomass materials; (c) ablative pyrolysis – characterized by rapid physical reaction of biomass materials on heated surfaces on short retention times; and (d) traditional pyrolysis – characterized by low temperatures and long retention times.

Table 1 shows the typical product distribution from the different modes of pyrolysis using wood.

Table 1. Typical product yields (dry wood basis) obtained by different pyrolysis modes.

| Mode | Conditions | Liquid (%) | Char (%) | Gas (%) |
|---|---|---|---|---|
| Fast | Moderate temperature, around 500°C, short hot vapor residence time ~ 1 s | 75 | 12 | 13 |
| Intermediate | Moderate temperature, moderate hot vapor residence time ~ 10–20 s | 50 | 20 | 30 |
| Slow | Low temperature, around 400°C, very long residence times | 30 | 35 | 35 |

Source: EIA (2007).

Flash pyrolysis of agricultural residue using plasma-heated, laminar-entrained flow reactor is described by Shuangning et al. (2005). This study investigates the volatilization characteristics of the biomass particles at flash heating rates using wheat straw and corn stalks. A first-order kinetic model was developed to predict relevant process parameters and reaction products.

A laboratory study of cotton-gin waste pyrolysis was conducted by Zabaniotou et al. in 2000. The effect of temperature (350–800°C) on the product yields was determined by using a captive sample batch reactor heated at a rate of 80–100°C $s^{-1}$. It was found that high temperature favored gas production (i.e., CO, $CH_4$, $CO_2$, $H_2$, and $C_2H_4$) while it gave very low yields of tar and liquid (almost negligible) which, they say, was probably due to slow pyrolysis process.

2.2. *Bio-Oil Production*

The condensable gas also known as pyrolytic oil or bio-oil is considered the most interesting product of pyrolysis because it has a high energy density, may be used directly as a liquid fuel, can be added to petroleum refinery feedstocks, and can be catalytically upgraded to high-quality transport fuels. Bio-oil may also be stored or transported from the plant for later use (Putun et al., 1999). Bio-oils are composed of high amounts of water and different chemicals derived from the depolymerization and fragmentation of cellulose, hemicelluloses, and lignin (Zhang et al., 2006). Studies on fast pyrolysis of cellulosic biomass are focused primarily on the production of bio-oil as an aggregate fuel. There were very few studies made to upgrade the bio-oil into transport fuels. Weiming et al. (2005) reviewed the different pyrolysis studies done using agricultural biomass that resulted in the development of at least five different variations of the pyrolysis process. Most of the pyrolysis studies have shown that the product profile depends mostly on the type of biomass used rather than on the pyrolysis conditions (Barth et al., 1999). Fluidized bed pyrolysis technologies offer a better alternative because of their high throughput, superior heat and mass transfer characteristics, low tendency to clogging, and ability to maintain nearly constant temperature throughout the reactor (Lin and Yen, 2005). A fluidized bed reactor was used in the fast pyrolysis mode to produce liquid fuel from wood feedstock and rice straw (Lua et al., 2004). Studies to upgrade bio-oil into transport fuels made use of numerous solid (acid or base) catalysts (Zhang et al., 2006). However, steam pyrolysis was found to be a more superior process due to higher oil yield and the increased

removal of volatile products (Putun et al., 2006). Other studies focused on catalytic conversion of oil into liquid fuels using novel zeolite catalysts, notably the HZSM-5 and HY type catalysts (Adjaye and Bakhshi, 1995). The synthesized mesoporous molecular sieve, MCM-41, has been shown to catalyze the selective formation of linear hydrocarbons in the $C_{13}$ and $C_{17}$ range (Twaiq et al., 2003). The selectivity for particular liquid hydrocarbons such as gasoline, kerosene, or diesel was found to be dependent on the pore size and the surface area of the catalyst. HY and H-mordenite catalysts could be used to generate hydrocarbons within the kerosene boiling point range. Silicalite and HZSM-5 could be used to generate hydrocarbons within the gasoline boiling point range (Adjaye and Bakhshi, 1995).

The controlled thermal conversion of swine manure produced raw oil products that could be used as fuel. Result showed that the viscosity and benzene solubles were greatly influenced by the operating temperature and the type of process gases produced (He et al., 2001).

Catalyzed pyrolysis is fast gaining popularity in the thermochemical conversion process especially for lignocellulosic biomass. Encinar et al. (1997) conducted a catalytic pyrolysis of grape and olive bagasse using sulfuric and phosphoric acids under different conditions. A cylindrical stainless steel reactor with a ceramic furnace was used to pyrolyze the raw materials from 400 to 800°C. They observed that in the presence of catalysts, char fraction was increased while the liquid decreased. However, the gases (i.e., $H_2$, CO, $CO_2$, and $CH_4$) were unaffected except when Fe or Al was used. The influence of temperature was also determined where an increase in temperature led to

decreased solid yield and increased gas yield; the optimum temperature was determined at 600°C. In a parallel study, Putun et al. (2005) used catalyzed pyrolysis on air-dried cottonseed cake using natural zeolite content while varying the pyrolytic temperature, zeolite content, and sweeping gas flow rate. A 316 stainless steel Heinze retort was used as a reactor heated by an electric furnace. The temperature in the bed was controlled by a thermocouple. Tar condensation was avoided by providing heat along the connecting pipes. The maximum liquid produced was 31% at a pyrolysis temperature of 550°C with a sweeping gas flow rate of 100 $cm^3$ $min^{-1}$ in the presence of clinoptilolite molecular sieve. It was also found that increasing the pyrolysis temperature increased the yield of conversion while decreasing the yield of char, whereas increasing the zeolite content resulted with a little change in the pyrolysis conversion.

Tsai et al. (2006B), on the other hand, used induction heating for the lab-scale pyrolysis system of rice husk and were able to produce pyrolytic oils and chars. The process parameters that were examined include pyrolysis temperature, heating rate, holding time, nitrogen gas flow rate, condensation temperature, and particle size on the pyrolysis product yields and their chemical compositions. A horizontally tubular reactor was used for the fixed-bed fast pyrolysis experiment. The heating rate used was 100–500°C in the high-frequency generator. Like in the previous studies, the char yield had a declining trend as the final pyrolysis temperature is increased while the oil yield also increased. The optimum condensation temperature for effectively collecting gas products was found at -10°C. The optimal oil yield of >40% was achieved at the pyrolysis

temperature of >500°C, heating rate of >200°C $s^{-1}$, holding time of >2 min, condenser temperature of <-10°C, and particle size of <0.5 mm.

2.3. *Char By-Products*

The char by-products of pyrolysis have relatively high carbon content and heating value and there are potential high value products that could be generated from this product output. Perhaps the most popular product would be the conversion of the high carbon char into activated carbon.

Activated carbon, a widely used adsorbent, is mainly composed of carbonaceous material with high surface area and porous structures (Abdel-Nasser and El-Hendawy, 2005). Raw materials for its production are chosen depending on their price, purity, potential extent of activation, and stability of supply (Kim, 2004). Numerous studies have been devoted to the preparation of low-cost high-quality carbon adsorbents for treatment and purification of water, air as well as various chemical and natural products (Abdel-Nasser and El-Hendawy, 2005; Budinova et al., 2006). The raw materials being used are usually carbonaceous materials such as wood (Ahmad et al., 2006), coal (Lozano-Castello et al., 2005), nut shells (Lua et al., 2004), husks (Baquero et al., 2003), and most agricultural byproducts materials (Abdel-Nasser and El-Hendawy, 2005; Duran-Valle et al., 2005; Budinova et al., 2006).

Granular activated carbon was produced from turkey manure (Lima and Marshall, 2005). Steam activation was used to improve the adsorptive abilities of the raw char. The turkey litter and cake samples were pyrolyzed at the laboratory using bench

tube furnace at 700$^{o}$C under nitrogen gas flow rate of 0.1 $m^3$/h for 1 h before activation. Chars were activated at 800$^{o}$C for 15, 30, 45, and 60 min at various steam flow rates of 1, 3, and 5 ml $min^{-1}$. Activated products were found to be a good material for metal adsorption.

2.4. *Non-Condensable Gaseous Products*

The predominant gaseous products of pyrolysis process are CO and $H_2$. The two gases are collectively called synthesis gas, syngas, or producer gas. These gaseous products could be reformed into liquid transport fuels via steam-reforming (non-catalytic) and catalytic-reforming processes. One of the most popular catalytic liquid-reforming processes is the Fischer-Tropsch (FT) process. This process was developed in Germany during World War II. The process uses metal-based catalysts to form products for transport fuels. The disadvantages of the FT process include the following: poisoning of the catalysts by sulfur and other metals and the wide range of products produced that comprised long-chain paraffins which must be further converted into shorter-chain transport fuels. Thus, newer catalysts such as hybrid zirconia are now being used for the FT process.

Some studies on controlled non-catalytic on-line pyrolysis of vegetable oils showed that pyrolysis may yield hydrocarbon products in the $C_3$-$C_{16}$ range as shown in Table 2 (Fortes and Baugh, 1999). A large percentage of the compounds (nearly 50%) can be considered within the aviation fuel range. Further upgrading using catalysts may improve hydrocarbon product yield. A study reported that the hydrogen to carbon ratio

(H/C ratio) has to be optimized for proper production of specific hydrocarbon compounds (Putun et al., 2006). There may be a need to provide additional hydrogen during the pyrolysis process to improve hydrocarbon production.

Table 2. Constituents identified from pyrolysis of Macauba nut oils.

| | Main products (aldehyde, alkene, carboxylic acid, diene) | Secondary products (cycloalkane, alkane, alkyl benzene) | Tertiary products (alcohols, etc.) |
|---|---|---|---|
| Macauba nut oil | 59–74% | 24–37% | 5–7% |
| Macauba pulp oil | 71–79% | 19–26% | 3–4% |

# 3. METHODOLOGY

## 3.1. *Initial Pyrolysis Experiment*

### 3.1.1. *Sample Preparation*

The samples of CGT used in the first experiment were obtained from the Varisco Court Gin Company located at Bryan, Texas. The CGT was a mixture of small pieces of ground cotton burrs, leaves, and stalks in various shapes and sizes. A large portion of the sample was cotton lint. Because of this wide variability in the composition of cotton-gin trash, it was difficult to study particle size variation in this experiment.

The moisture content (MC) of the air-dried cotton-gin trash was determined following ASTM method E1756-95. The sample materials were oven-dried overnight (24 h) with the temperature set at 105 °C. The average MC (as-received, a.r.) was about 15% by weight (wt.%, dry basis). Values for the ultimate analysis of CGT from previous studies are listed in Table 3. After oven-drying, the CGT was ground in a laboratory mill with 6.0-mm (diameter of holes) sieve to achieve close to uniform particle sizes. A part of the processed CGT was used for the heating value determination using a Parr isoperibol bomb Calorimeter (Model No. 6200, Parr Instrument Company, Moline, IL).

Table 3. Proximate and ultimate analyses (wt.%, dry basis) and other properties of CGT.

| Reference | C | H | N | S | O | Ash | MC (a.r.) | HV ($kJ\ kg^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| Preliminary study | – | – | – | – | – | 11.3 | 15.0 | 16,580 |
| Zabaniotou et al. (2000) | 41.23 | 5.03 | 2.63 | ~0 | 34.0 | 13.3 | 6.0 | 15,780 |
| Lepori and Parnell (1989) | 43.82–45.97 | 4.62–4.85 | 2.95–2.04 | 0.43–0.45 | 32.61–34.23 | 11.88–12.46 | 0.0 | 15,480 |

3.1.2. *Pyrolysis Runs*

The prepared cotton-gin trash was pyrolyzed in a batch-type reactor made from a schedule 80 steel pipe, 0.9 m (3 ft) long with 7.62 (3 in.) internal diameter (ID). Two steel trays/containers (A) were made to fit the interior of the tubular reactor (B). The trays can hold a maximum load of approximately 250 g ground cotton-gin trash inside the reactor during pyrolysis. The horizontal Thermolyne™ tube furnace (C) (Model No. 79300, Barnstead International, Dubuque, IA), 55 cm (21.50 in.) in length and with a maximum of 7.62 cm (3.0 in.) in internal furnace diameter, provided the different temperature settings for pyrolysis, i.e., 600, 700, or 800°C.

Figure 1 shows the schematic diagram of the pyrolysis setup used in the experiment. The time period for the pyrolysis of each cotton-gin trash sample was also varied (30, 45, and 60 min) along with the varying temperature. Approximately 100 g (± 0.5 g) of the prepared CGT was loaded in the steel tray container for each run. The gaseous products produced during pyrolysis were directed to pass through a condenser (B), with 10.16-cm- (4.0-in.) diameter coils (0.5-in.-ID copper tube) and a total height of

46 cm (18.0 in.). The cooling water flow rate at the condenser was maintained at 1.875 l $min^{-1}$ while the temperature was maintained at approximately 17°C. The liquid condensates (bio-oil) were collected in a glass cold trap (D) that used crushed ice to maintain the temperature at around 0°C. The non-condensable gases were then collected and measured using the water displacement tanks (E and F).

3.1.3. *Char Heating Value Analysis*

After pyrolysis, the chars were collected, weighed, and stored in individual polyethylene (PET) bags. The amounts of liquid condensates and non-condensable gases were measured by volume. The heating values of the collected pyrolysis chars from each run were also determined using the bomb calorimeter described earlier.

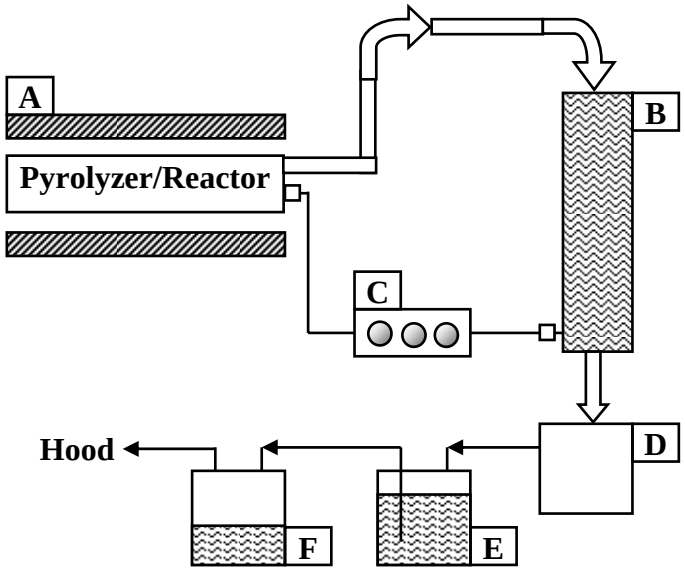


Figure 1. The preliminary pyrolysis setup. (A) Programmable tube furnace, (B) Condenser, (C) Thermocouple reader, (D) Liquid collector, and (E and F) Volume-displacement tanks.

### 3.2. *Modified Pyrolysis Test Runs*

#### 3.2.1. *Sample Preparation*

The feedstock, cotton-gin trash, was collected from a local ginning facility in El Campo, Texas. The feedstock was composed of different parts and pieces of the cotton plant and was consistent with the material used in the first experiment. The CGT was air-dried for about 3 days to reduce the initial moisture content and was fed into a laboratory mill with a 6-mm-diameter sieve. Due to the heterogeneity of the material, uniform particle sizes were difficult to achieve. The moisture content of CGT was determined in accordance with ASTM D 3173. A thermogravimetric method according to ASTM standards (E 1755 and E 3175) was used to conduct proximate analysis on the prepared sample. The Parr isoperibol bomb calorimeter (Model 6200, Parr Instrument Company, Moline, IL) was used for all heating value determination in accordance with ASTM D 2015.

#### 3.2.2. *Pyrolysis Runs*

The experimental setup was a laboratory batch pyrolysis setup similar to the first reactor, having a capacity of up to 250 g feedstock per test run. The schematic of the entire pyrolysis setup for CGT is shown in Figure 2. The pyrolyzer reactor was made of cylindrical steel (ANSI Schedule 80), 0.915 m (3 ft) in length with 7.366 cm (2.90 in) ID. The steel reactor was inserted in the tube furnace which is capable of temperature programming. A gas inlet port for nitrogen ($N_2$) was connected on one end of the reactor while an exit port for the pyrolysis gas was connected on the other end. Attached to the

gas exit port was a tar trap with filter paper followed by the condenser. The copper tubes connecting the reactor, the tar trap, and the condenser were insulated to prevent line condensation and minimize losses. The cooling water for the condenser was circulated by a water pump and was maintained at around 5–10°C. The liquid collector at the bottom of the condenser was submerged in an ice bath (at ~0°C) and was used to collect the condensable gases (bio-oil) and tar while the non-condensable gases were routed to a water trap (bubbler) to strip-off the remaining moisture. The non-condensable gases were then directed to the gas analyzer (Horiba Gas Analysis System, Horiba International Corp., Irvine, CA.) provided with non-destructive infrared (NDIR, Model VIA-300) detectors, thermal conductivity detector (TCD, Model TCA-31), and oxygen analyzer (Model PMA-200.), and into the exit ports. The two exit ports were used for gas sampling and for gas exhaust.

Steel trays were used to hold the sample inside the reactor and were also the receptacle for the char and ash after pyrolysis. Approximately 50 g fresh CGT was used for every run. Before the start of each run, $N_2$ was purged into the reactor at a rate of 1000 $cm^3$ $min^{-1}$ and maintained at that flow for about an hour to remove the air completely from all the components of the setup. The reactor was then heated from room temperature (approx. 25°C) until the desired temperature settings (500, 600, 700, and 800°C) using a fixed ramp rate of 1.5°C $s^{-1}$ and was held at that temperature for the required reaction time. After pyrolysis, the solid products (char and ash) were collected and weighed as well as the condensed gases (bio-oil); the non-condensable gases were

calculated by difference. The pyrolysis tests were done in triplicate and the average values were reported in this manuscript.

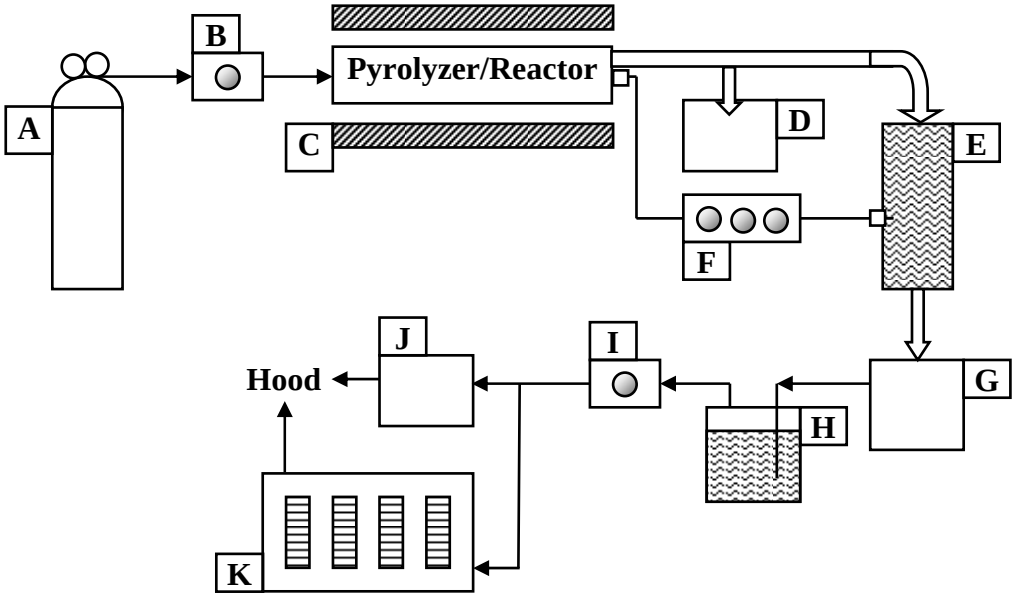


Figure 2. The modified pyrolysis setup used for CGT. (A) Purge gas ($N_2$), (B) Gas flow meter 1, (C) Digitally-controlled furnace, (D) Tar/moisture trap, (E) Condenser, (F) Thermocouple reader, (G) Liquid collector, (H) Moisture trap, (I) Gas flow meter 2, (J) Sampling/exhaust port, and (K) Gas analyzer.

3.2.3. *Compositional Analysis*

3.2.3.1. *Char Analysis*

The products of pyrolysis were collected, quantified, and analyzed after each test run. Proximate analysis was done to characterize the solid products (char and ash) and was performed according to ASTM standards mentioned earlier. The heating values were determined using the Parr isoperibol bomb calorimeter mentioned earlier.

3.2.3.2. *Gas Analysis*

The gaseous product composed mainly of $H_2$, CO, and $CO_2$, also known as synthesis gas (syngas) and total hydrocarbons (THCs), was analyzed by the on-line gas analyzer mentioned earlier. The yields of these major gases were quantified by calibration with standard gases of known concentration consisting of $H_2$, CO (balanced with $N_2$), $CO_2$ (balanced with air), $O_2$, and THC (balanced with air) (Praxair Specialty Gases, Austin, TX). The composition of the low–molecular weight hydrocarbons ($C_1$ to $C_6$) was determined using an SRI (Model 8610C) gas chromatograph (GC) equipped with an on-column injection system and two detectors: flame ionization detector (FID) and photo-ionization detector (PID). The column used was a non-polar MXT-1 (100 % dimethyl polysiloxane) capillary column, 60 m length, 0.53 mm ID. The calibration gas standard mixture used was composed of $C_1$ to $C_6$ paraffins (Scott Specialty Gases, Plumsteadville, PA) with analytical accuracy of ±5 %. Hydrogen and helium were used as carrier gas.

3.2.3.3. *Pyrolytic Oil Analysis*

The liquid product (bio-oil) was collected in a glass bottle and the filter paper soaked in dichloromethane and used as a tar trap was slowly evaporated at ambient temperature. The liquid product yield was determined by weighing the tarred glass bottle and filter paper. The pH of the bio-oil was measured using Fisher Scientific (Accumet Model 25) pH/ion meter to determine its corrosion properties. The bio-oil was decanted, vacuum-filtered through a 0.4-μm filter paper, and was centrifuged for 15 min to

separate the solids and some impurities from the bio-oil. The heating value of the prepared bio-oil was determined using the isoperibol bomb calorimeter mentioned earlier.

### 3.2.4. *Energy and Mass Balance*

The mass balance for CGT pyrolysis was performed by comparing the mass of the initial input biomass to the quantity of all the different output products (i.e., char, ash, bio-oil, tar, and syngas). Product losses were unavoidable, thus mass balance was done by means of difference while assuming 100% conversion. A simple energy balance was performed starting from material preparation (grinding) to pyrolyzer operation (programmable furnace). The energy content of the fresh cotton-gin trash was determined and was compared to the net energy content of the different pyrolysis products. The heating value of the gaseous product was computed based on the difference in heating values of the char and bio-oil from the heating value of the initial CGT.

# 4. RESULTS AND DISCUSSION

## 4.1. *Properties of Cotton-Gin Trash*

The results of the proximate analysis for the fresh CGT sample are shown in Table 4. The average yields were obtained from triplicate experiments with a standard deviation of less than 0.5 wt.%. The properties of the fresh CGT were very consistent with the values found in the literature (Zabaniotou et al., 2000; Lepori and Parnell, 1989). The actual heating value determined using the bomb calorimeter was around 5.6% lower than the computed heating value based on the equation suggested by Parikh et al. (2004) and was about 0.13% different from the equation suggested by Demirbas (1997) (see Appendix B).

Table 4. Proximate analysis of CGT as-received (a.r.) and other properties.

| Parameter[a] | Value (wt. %)[b] | $\sigma$ | HHV[c] (MJ kg$^{-1}$) | HHV[d] (MJ kg$^{-1}$) |
|---|---|---|---|---|
| Ash | 15.43 | 0.20 | 15.48 | 16.40 (a) |
| VM | 68.88 | 0.26 | | 15.46 (b) |
| FC | 15.69 | 0.10 | | |
| MC (wb) | 9.70 | 0.17 | | |
| MC (db) | 10.74 | 0.21 | | |
| **Total** | 100.00 | | | |

[a]VM = volatile matter, FC = fixed carbon, MC = moisture content (wet basis/ dry basis) as-received.
[b]By weight percent dry basis.
[c]HHV = measured high heating value.
[d]HHV = computed high heating value based on (a) Parikh et al. (2004) and (b) Demirbas (1997).

## 4.2. *Initial Test Results*

### 4.2.1. *Effect of Pyrolysis Temperature*

Figures 3, 4, and 5 show the effects of the different temperature settings on the product yields at pyrolysis periods of 30, 45, and 60 min, respectively, for the pyrolysis of cotton-gin trash with the horizontal tube batch reactor. All of the yields were expressed in weight percentage based on the original sample and were obtained from the average yields from duplicate experiments. Figure 3 (A) shows that the char production has decreased by almost 10 wt.% as the pyrolysis temperature increased from 600 to 800°C. On the other hand, the liquid production has increased by more than 12 wt.% while the gas production also increased by more than 13 wt.%. The increasing or decreasing trends of the solid, liquid, and gaseous products of pyrolyzed cotton-gin trash were consistent with the trends of other pyrolyzed biomass reported on the literature (Putun et al., 1999; Caglar and Demirbas, 2000; Boateng et al., 2006; Tsai et al., 2006B).

According to Boateng et al. (2006), char yield is a function of pyrolysis temperature and this explains the decline in char production with increased temperature that was observed in all of the samples after pyrolysis. The increasing yields of liquid and gaseous products with increasing temperature could be attributed to the conversion of biomass to volatile materials at high temperatures (Putun et al., 1999). It was also expected that, at very high pyrolysis temperature, liquid production will decrease while gas production will increase. This could be explained by the rapid devolatilization of the cellulosic and hemicellulosic materials at very high temperature according to Putun et al. (1999).

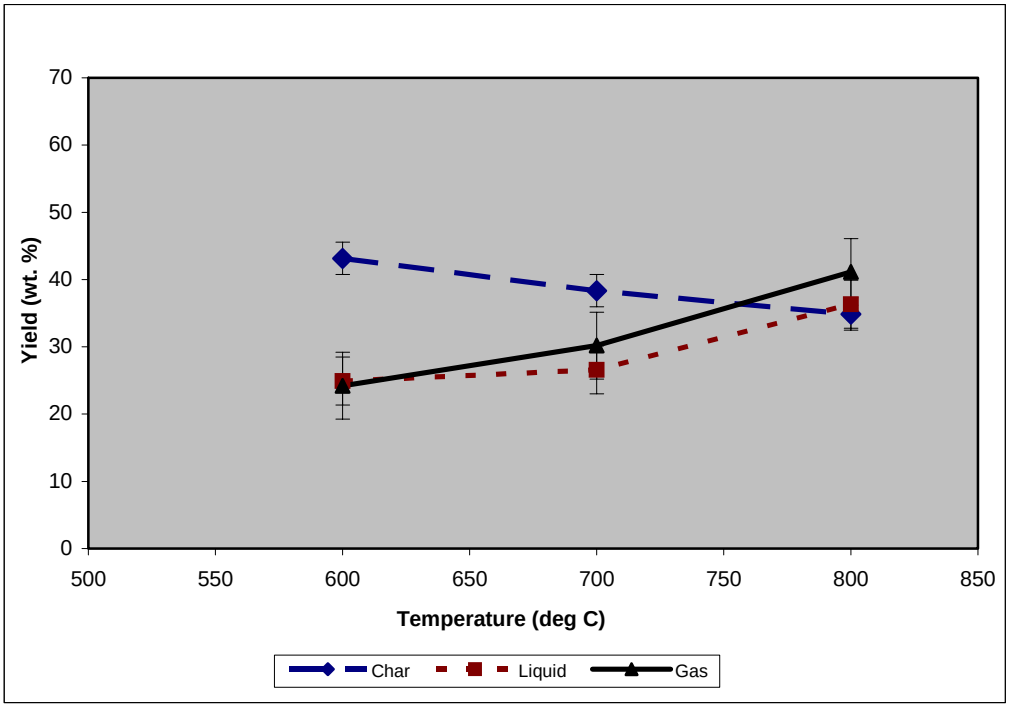


Figure 3. Product yields at different temperatures with pyrolysis time of 30 min.

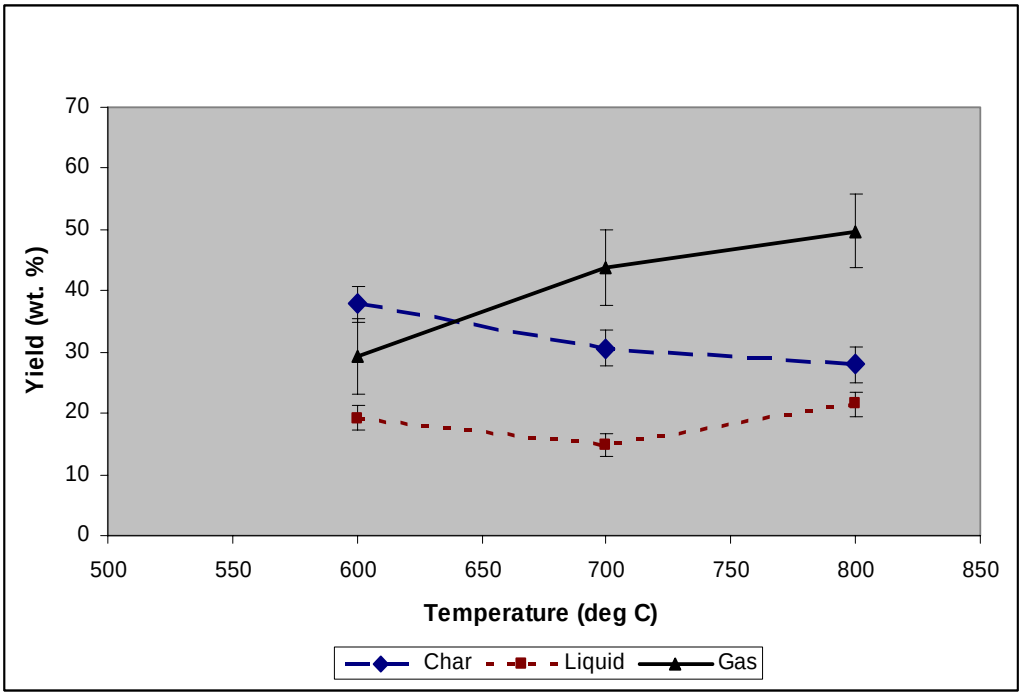


Figure 4. Product yields at different temperatures with pyrolysis time of 45 min.

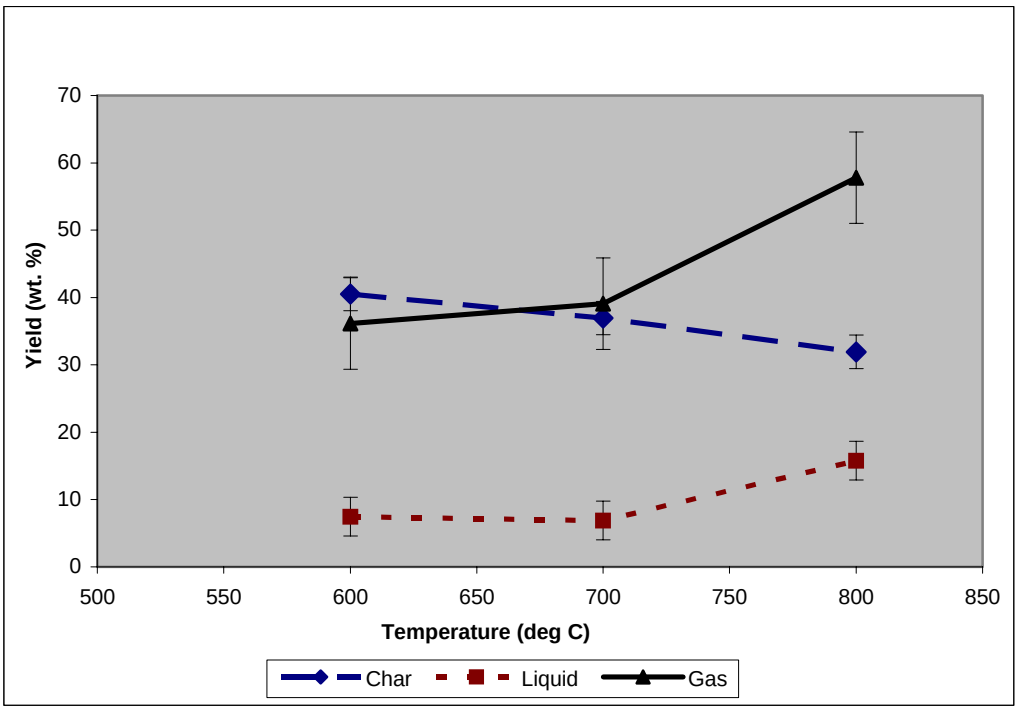


Figure 5. Product yields at different temperatures with pyrolysis time of 60 min.

4.2.2. *Effect of Reaction Time*

The effects of increasing pyrolysis time on the solid or char, liquid, and gas productions were also observed during the experiment. Figure 6 shows the solid production against the pyrolysis time at different temperature settings (600, 700, and 800°C). It can be noted that while the pyrolysis time was increased from 30 to 60 min, the solid production was almost constant but had a slight decrease at time equal to 45 min for all the temperature settings. The maximum solid yield of 40 wt.% was observed at the temperature equal to 600°C, followed by 700°C (38 wt.%); the temperature setting of 800°C had the least solid production (32 wt.%). One possible reason for having a higher solid production with the 600 °C setting is that the lower

temperature and time (30 min) settings were not enough to completely pyrolyze all the cotton-gin trash input, especially those in the middle portion of the sample. This was further supported by the observed heating values of the char collected from each sample. The heating values of the char at the pyrolysis temperature of 600°C were considerably lower (approx. less than 6 MJ $kg^{-1}$) compared to the heating values of char at 700°C and were closer to the heating values of the "unpyrolyzed" (raw) cotton-gin trash which was around 16.60 MJ $kg^{-1}$. On the other hand, with the highest temperature setting at 800°C, the solid production started to decline. This could be because, at increasing temperature, coupled with longer pyrolysis time, most of the char is further decomposed and converted to volatile gases (Putun et al., 2005). The final solid product would then be composed of char with high ash content. This could also explain why the char collected at 800°C have lower heating values than those collected at 700°C (fig. 9).

In figure 7, a longer pyrolysis time resulted to higher gaseous product yield for almost all the temperature settings. The highest gas yield (57.80 wt.%) was observed at 800°C and 60-min settings followed by 700°C settings and the least (24.23 wt.%) was from the 600°C and 30-min setting. As stated earlier, longer pyrolysis time and higher temperature favor gas production due to further conversion of biomass to volatile gases. Moreover, the gaseous products produced were determined to be highly combustible and could be readily used or stored in canisters. The gaseous products contain high concentrations of producer gas (syngas) composed of CO, $H_2$, and other low–molecular weight hydrocarbons which could be used as primary fuels for direct combustion according to Boateng et al. (2006). The amounts of liquid produced from the pyrolysis of

cotton-gin trash were very low, although figure 8 still shows an inverse relation with increasing time for all the temperature settings. It was also determined that a major portion of the condensed liquid products from each sample was composed of water as verified by its density and heating value.

Formation of a thick, black tar stuck on the walls inside the tubular reactor was observed after every run while some portions of the tar can also be seen mixing with the condensed liquid products. No other procedure was done to minimize the tar build up and any amount of tar produced was just treated as errors or losses.

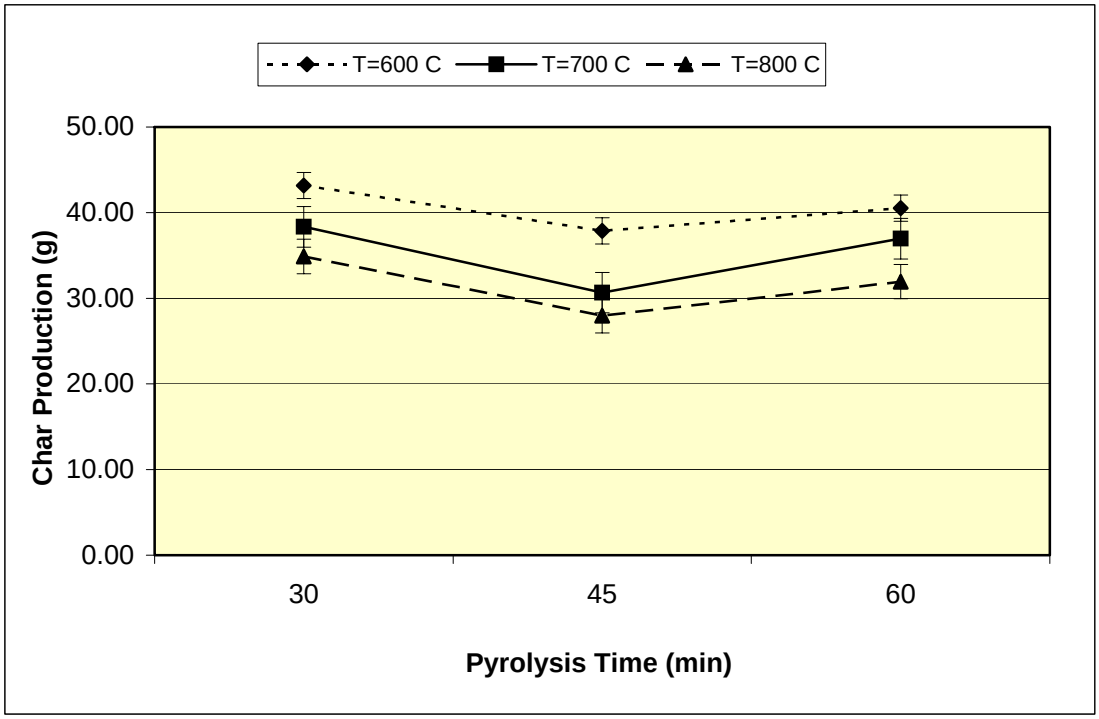


Figure 6. Solid (char) product yield at different temperatures with increasing pyrolysis time.

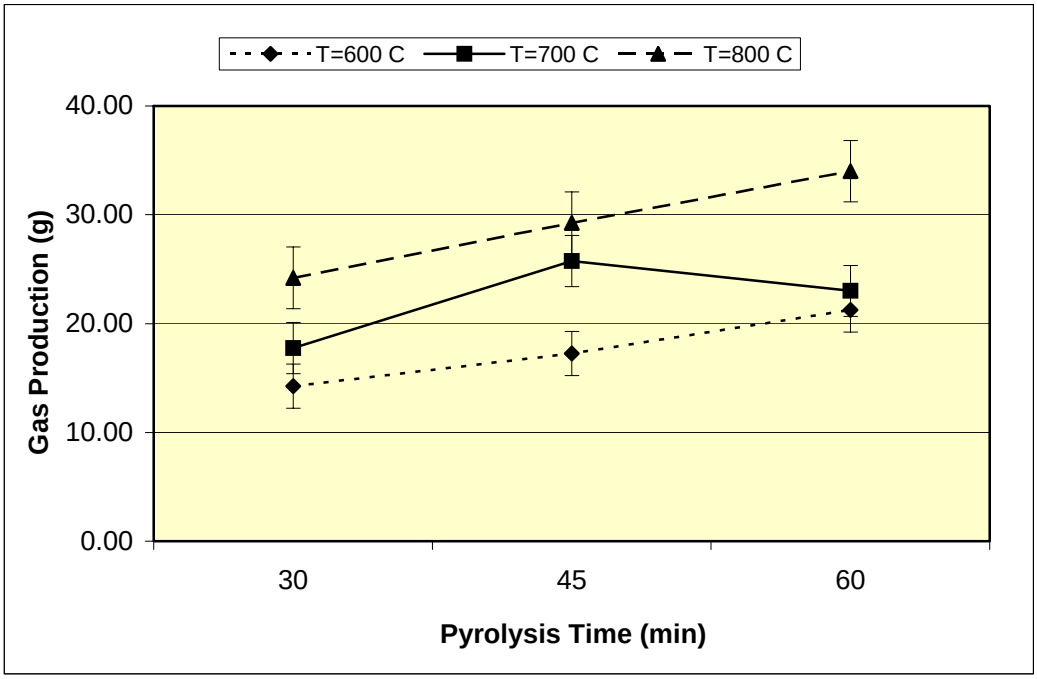


Figure 7. Gas product yield at different temperatures with increasing pyrolysis time.

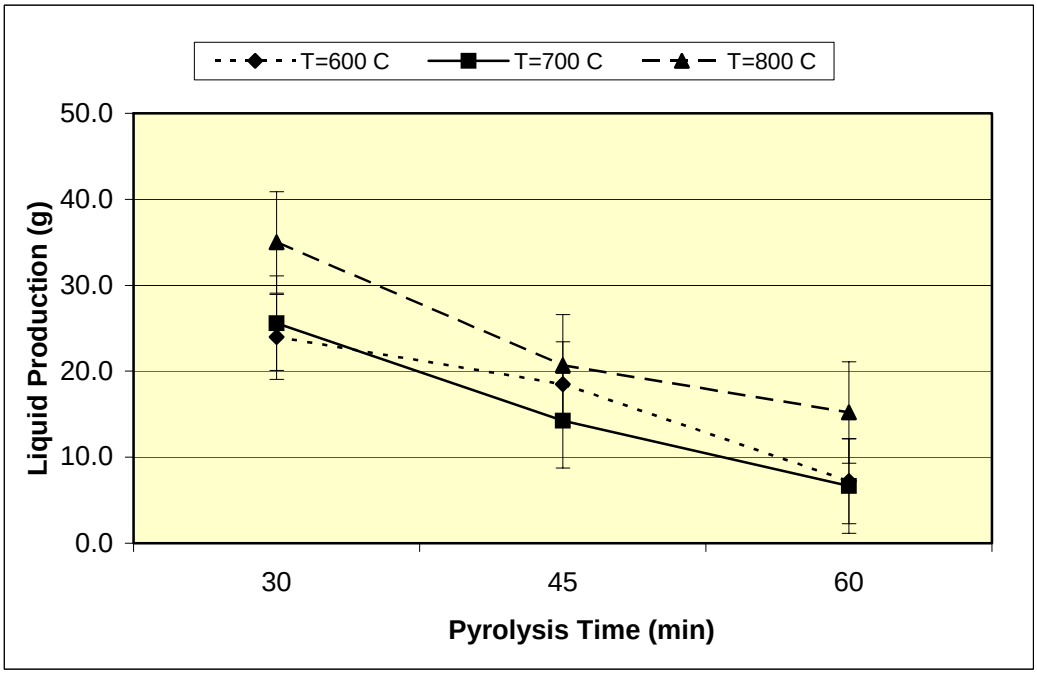


Figure 8. Liquid product yield at different temperatures with increasing pyrolysis time.

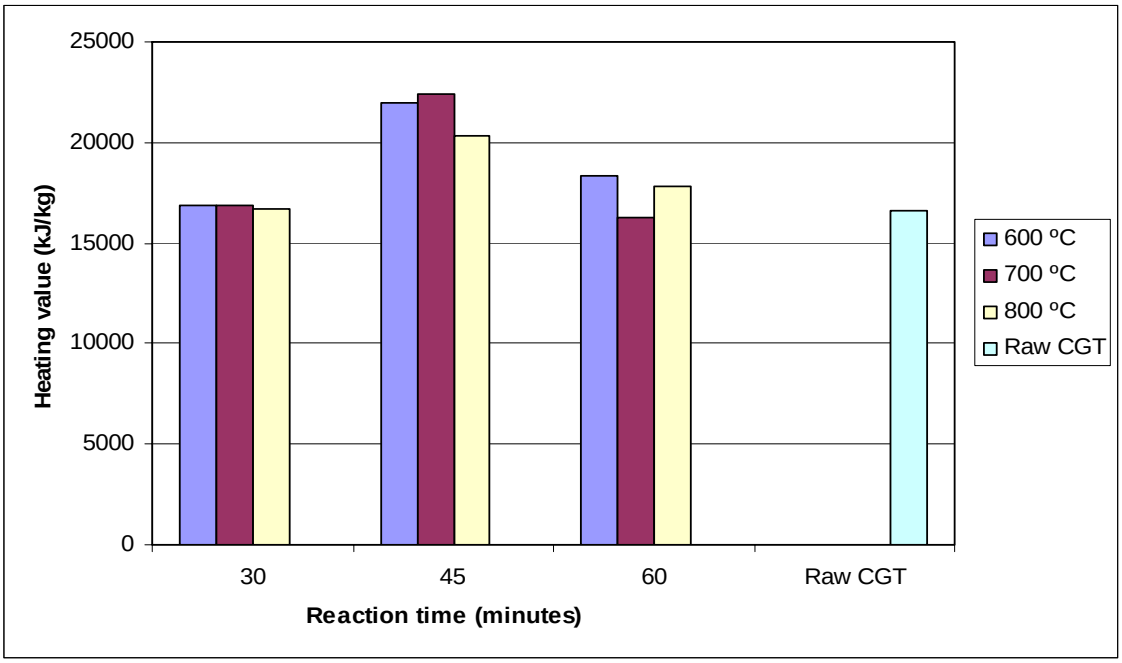


Figure 9. The measured heating values of the raw and pyrolyzed CGT samples.

## 4.3. *Modified Pyrolysis Test Results*

### 4.3.1. *Product Yields*

The prepared CGT sample was pyrolyzed at different temperatures (500, 600, 700, and 800°C) using a fixed reaction time of 30 min and purge gas ($N_2$) flow rate of 1000 $cm^3$ $min^{-1}$. The products of pyrolysis (Appendix A), solid and liquid, were directly quantified by gravimetric method while the total gas weight was calculated based on weight difference assuming (1) no losses and (2) a fixed 20 wt.% product loss. The average yield in mass percent for each pyrolysis product is shown in Table 5. After each run, the pyrolyzer was left to cool down to below 80°C and then the solid product or char was removed and transferred immediately into a pre-weighed PET bag. The bag was tightly sealed to prevent moisture absorption. The highest char production of 38

wt.% was determined at 500°C while the lowest char of 35 wt.% was determined at 800°C. The char yield was reduced by about 9 wt.% as the temperature was raised from 500 to 800°C. The amount of char produced at 500°C was also determined to be significantly higher ($\alpha = 0.05$) than the yields of char at the succeeding temperatures. According to Williams and Nugranad (2000), the decrease in char yield with increasing temperature could either be due to greater primary decomposition of the biomass at higher temperatures or through secondary decomposition of the char residue.

The secondary decomposition of the char at higher temperatures may lead to an increase in non-condensable gas production as observed in the experiment. The highest gaseous product yield of 35 wt.% was determined at 800 °C but the lowest (32 wt.%) was observed at 600°C. There could be two major possible reasons as to why the gas yield at 500°C was unusually high. First, because the gaseous products were determined only by difference, the amount of losses could have been significantly high and should be subtracted from the yield of the gaseous product. Second, there could have been a significant mechanical loss during the quantification of the liquid products. Ignoring the gas yield at 500°C, the gas production significantly increased ($\alpha = 0.05$) from 600 to 800°C and is consistent with the results in the literatures (Putun et al., 1999; Williams and Nugranad, 2000; Zabaniotou et al., 2000).

The improved pyrolysis process resulted to an increased liquid or bio-oil production of up to 30 wt.% which was not determined in previous studies using CGT as biomass material (i.e., Zabaniotou et al., 2000). The tar trap positioned immediately after the reactor and subjected under room temperature (ca. 23°C) may have resulted to the

quick condensation of the moisture and tar after leaving the reactor, which largely contributed to the bio-oil yield. It was observed during pyrolysis that the outside temperature of the tar trap remained low, enough to cause immediate water condensation before the remaining gases passed through the condenser. Only a very small amount of liquid (almost negligible) was collected after passing through the condenser. The bio-oil yield significantly increased from 500 to 600°C and significantly decreased from 600 to 700°C. According to Putun et al. (1999), rapid devolatilization of cellulose and hemicellulose occurs at pyrolysis temperature as low as 400°C. In addition, the secondary tar destruction at higher temperatures also causes a decrease in the liquid while the gas yield increases. Figure 10 shows the general trend for char, bio-oil, and gaseous production as affected by increasing temperature.

Table 5. Product yield from the pyrolysis of cotton-gin trash (wt. %).

| Temperature (°C) | Solid | Liquid | Gas[a] | Gas[b] | Losses[c] |
|---|---|---|---|---|---|
| 500 | 38.25 | 27.38 | 34.37 | 27.65 | 6.91 |
| 600 | 37.40 | 30.65 | 31.95 | 25.56 | 6.39 |
| 700 | 36.32 | 29.69 | 33.99 | 27.19 | 6.80 |
| 800 | 35.08 | 29.65 | 35.27 | 28.22 | 7.05 |

[a]Determined by difference (no losses).
[b]Wt. % of gas assuming 20 wt. % losses.
[c]Losses fixed at 20 wt. %

4.3.2. *Char Analysis*

The char produced from pyrolysis of CGT was characterized by proximate analysis and the higher heating value was measured using bomb calorimeter. Based on

the proximate analysis, it was observed that the volatile matter significantly decreased along with char production while the ash content significantly increased. The volatile matter decreased by about 72 wt.% and the ash increased by about 30.5 wt.% from 500 to 800°C. The ash content of char is rather high (28–38 wt.%) which is much higher than coal. Both data were statistically tested at $\alpha = 0.05$. The heating value of the char at different temperatures was also measured and determined to be not significantly different ($\alpha = 0.05$) from each other, although the highest heating value (ca. 22 MJ $kg^{-1}$) was recorded at 700°C and the lowest (ca. 20 MJ $kg^{-1}$) was at 500°C. On the other hand, the moisture content of the char was not measured and assumed to be negligible. The complete results of the proximate analyses for char can be found in Table 6.

Table 6. Proximate analyses for solid products from CGT pyrolysis at different temperatures.

**A.** Temperature: 500°C

| Parameter[a] | Value (wt.%)[b] | HHV[c] (MJ $kg^{-1}$) | HHV[d] (MJ $kg^{-1}$) |
|---|---|---|---|
| Ash | 28.99 | 19.23 | 20.57 |
| VM | 24.10 | | |
| FC | 46.91 | | |
| | 100.00 | | |

**B.** Temperature: 600°C

| Parameter[a] | Value (wt.%)[b] | HHV[c] (MJ $kg^{-1}$) | HHV[d] (MJ $kg^{-1}$) |
|---|---|---|---|
| Ash | 34.75 | 20.33 | 19.15 |
| VM | 21.22 | | |
| FC | 44.02 | | |
| | 100.00 | | |

Table 6 continued.

**C.** Temperature: 700°C

| Parameter[a] | Value (wt.%)[b] | HHV[c] (MJ $kg^{-1}$) | HHV[d] (MJ $kg^{-1}$) |
|---|---|---|---|
| Ash | 36.53 | 21.64 | 20.40 |
| VM | 11.77 | | |
| FC | 51.70 | | |
| | 100.00 | | |

**D.** Temperature: 800°C

| Parameter[a] | Value (wt.%)[b] | HHV[c] (MJ $kg^{-1}$) | HHV[d] (MJ $kg^{-1}$) |
|---|---|---|---|
| Ash | 37.83 | 19.70 | 20.93 |
| VM | 6.81 | | |
| FC | 55.36 | | |
| | 100.00 | | |

[a]VM = volatile matter, FC = fixed carbon, MC = moisture content (wet basis/ dry basis) as-received.
[b]By weight percent dry basis.
[c]HHV = measured high heating value.
[d]HHV = computed high heating value based on Parikh et al. (2004).

4.3.3. *Gaseous Product Analysis*

Table 7 shows the major composition of the gaseous products from the pyrolysis of CGT at different temperatures. The data reported were based on the collected gas under a $N_2$-rich atmosphere. According to Encinar et al. (2000), the escaping vapors during pyrolysis interact with the biomass and forms char through exothermic reactions. The $N_2$ flow inside the reactor facilitates the movement of these vapors and removes it to minimize secondary reactions such as cracking and char formation. A sample volume of pyrolysis gas was being pumped into the gas analyzer per minute and ejected to the exhaust hood after running through the analyzer. The analyzer recorded the gas concentration in millivolts (mV) while the data logger converted the volt readings into volume concentration (%). The average molecular weight ($MW_{ave}$) of the gaseous

product at each temperature was calculated based on the average concentration of each gaseous component in the sample (table 8). Because the sum of all gas concentrations in one sample was not 100%, it was assumed that the remaining part should be the purge gas or $N_2$ and the water in the gas was assumed to be zero because of the moisture trap (table 7). It was further assumed that $N_2$ did not form a significant amount of $NO_x$ during the process. The $MW_{ave}$ of the gas decreased with increased pyrolysis temperature. The highest $MW_{ave}$ of 30 g $mol^{-1}$ was observed at 500°C while the lightest was around 27 g $mol^{-1}$ at 800°C. The average gas density also decreased with increased pyrolysis temperature as affected by the decrease in $MW_{ave}$.

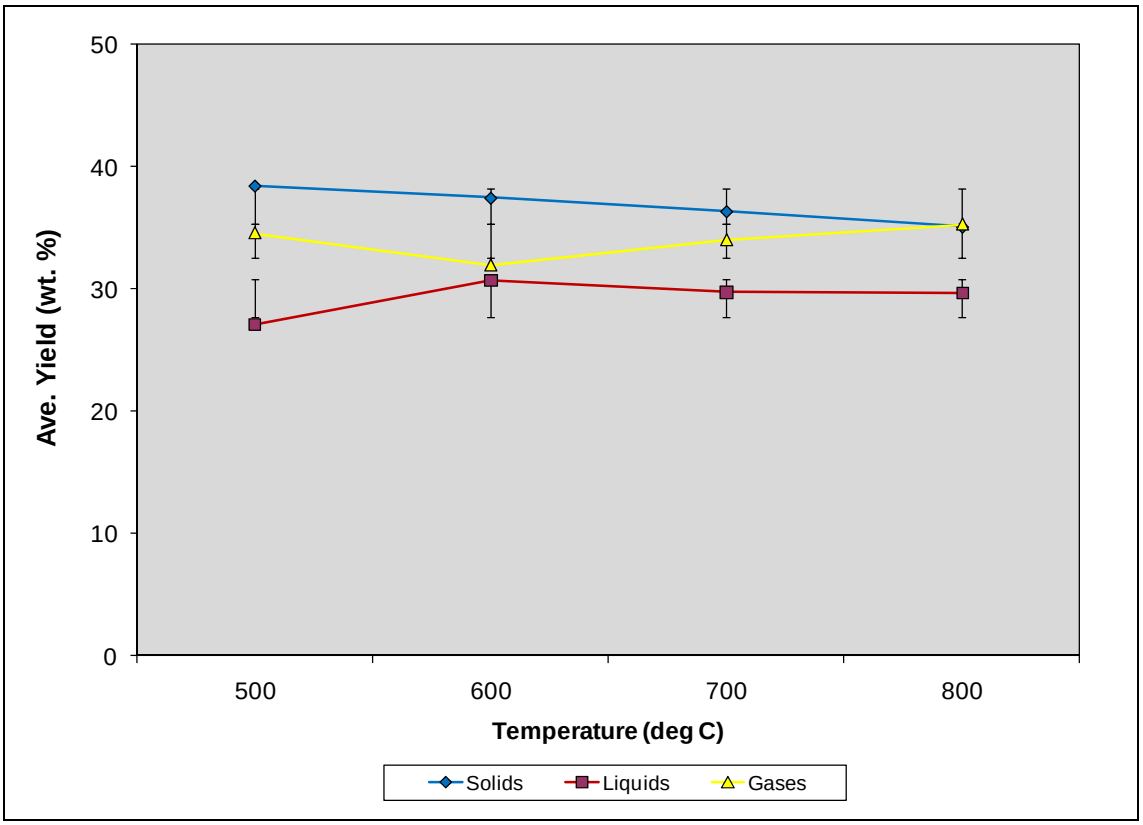


Figure 10. The distribution of the different products of pyrolysis (solid, liquid and gas) from CGT at different reaction temperatures.

Table 8 summarizes the estimated average molecular weight, density, and volume of the synthesis gas produced at each pyrolysis temperature settings. As state earlier, the gas production (GP) generally increase with temperature and the highest gas production of approximately 360 $m^3$ $kg^{-1}$ of CGT was determined at the highest temperature (800°C).

Gas analysis using the on-line analyzer with NDIR and TC detectors revealed the concentrations of CO, $CO_2$, THC, $O_2$, and $H_2$. The concentrations of CO, THC, and $H_2$ in the gas generally increased (Zabaniotou et al., 2000) as the temperature was increased from 500 to 800°C but $CO_2$ showed otherwise. The concentration of $CO_2$ has decreased by almost 60% from 500 to 800°C. This could have a considerable contribution to the decrease in $MW_{ave}$ of the gaseous product. The THC was analyzed in a gas chromatograph equipped with FID (Appendix D). Although the THC significantly increased from 500 to 700°C, it was observed that, when the temperature increased, the yield of lower–molecular weight hydrocarbons (HCs) was the one that increased significantly and that of higher–molecular weight HC actually either decreased or had no significant change. The observation was consistent especially from 600 to 800°C. This could also have affected the $MW_{ave}$ of the gas.

The major composition (vol.%) of the hydrocarbons ($C_1$ to $C_6$) is presented in figure 11 (see Appendix C). Methane ($C_1$), ethane ($C_2$), and propane ($C_3$) generally dominated the HC in most pyrolysis temperature although pentane ($C_5$) showed unusually high volume percentage at 600 and 700°C. Methane has the highest percent volume in all pyrolysis runs and composed almost 50% of the THC at 800°C.

Table 7. Major composition of the pyrolysis gas at different temperatures (mol%).

| Temperature (°C) | CO | $CO_2$ | THC | $O_2$ | $H_2$ | $N_2$ |
|---|---|---|---|---|---|---|
| 500 | 2.60 | 8.54 | 3.00 | 1.46 | 0.24 | 84.16 |
| 600 | 2.29 | 7.52 | 6.60 | 1.67 | 2.62 | 79.30 |
| 700 | 2.58 | 5.74 | 8.55 | 0.31 | 7.36 | 75.45 |
| 800 | 4.63 | 3.66 | 4.76 | 0.03 | 7.07 | 79.85 |

Note: THC = total hydrocarbon. Purge gas ($N_2$) was measured by difference, $H_2O$ ~ 0.

Table 8. Pyrolytic gas production from CGT.

| Temperature (°C) | MW (g $mol^{-1}$) | $\rho$ (kg $m^{-3}$) at STP | $M_{ave}$ (g) | $V_G$ ($m^3$) | $V_G$ (l) | GP (l $kg^{-1}$) |
|---|---|---|---|---|---|---|
| 500 | 30.0s60 | 1.229 | 17.29 | 0.0141 | 14.072 | **281.27** |
| 600 | 29.682 | 1.213 | 14.69 | 0.0121 | 12.105 | **241.82** |
| 700 | 27.908 | 1.141 | 19.31 | 0.0169 | 16.928 | **338.52** |
| 800 | 27.033 | 1.105 | 19.98 | 0.0181 | 18.086 | **361.59** |

Note: MW = average molecular weight, $\rho$ = density, STP = standard condition for temperature and pressure (25°C, 101.325 kPa), $M_{ave}$ = average mass (by difference), $V_G$ = gas volume, GP = gas production per kg of CGT (see Appendix B).

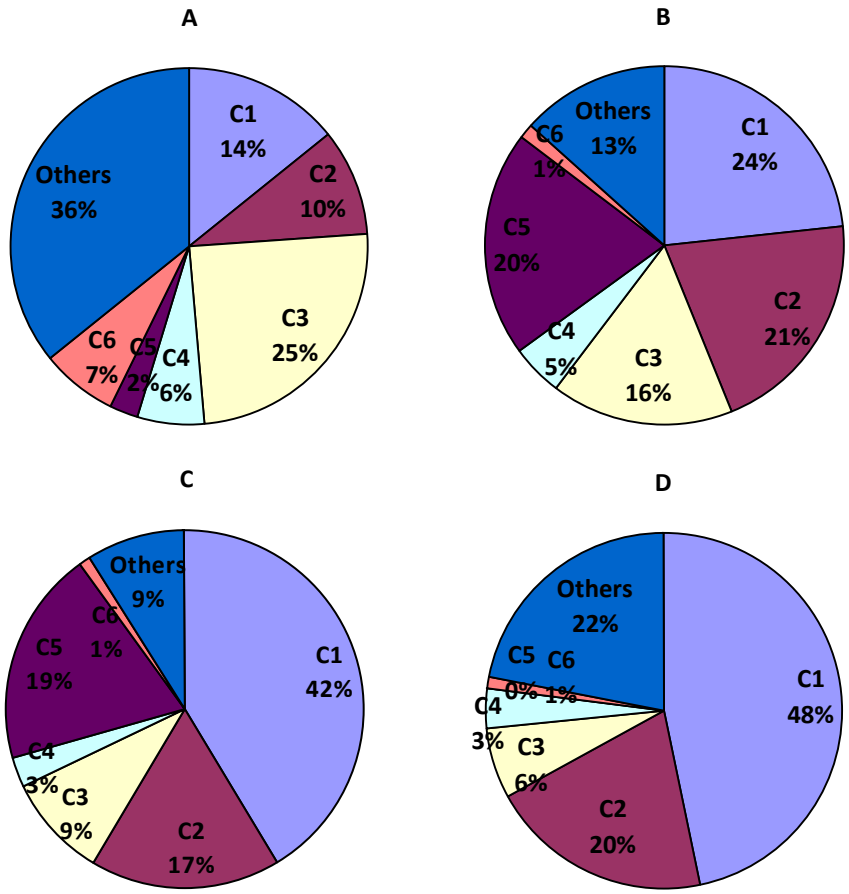


Figure 11. Major composition of the total hydrocarbons in the gaseous product at (A) 500°C, (B) 600°C, (C) 700°C, and (D) 800 °C.

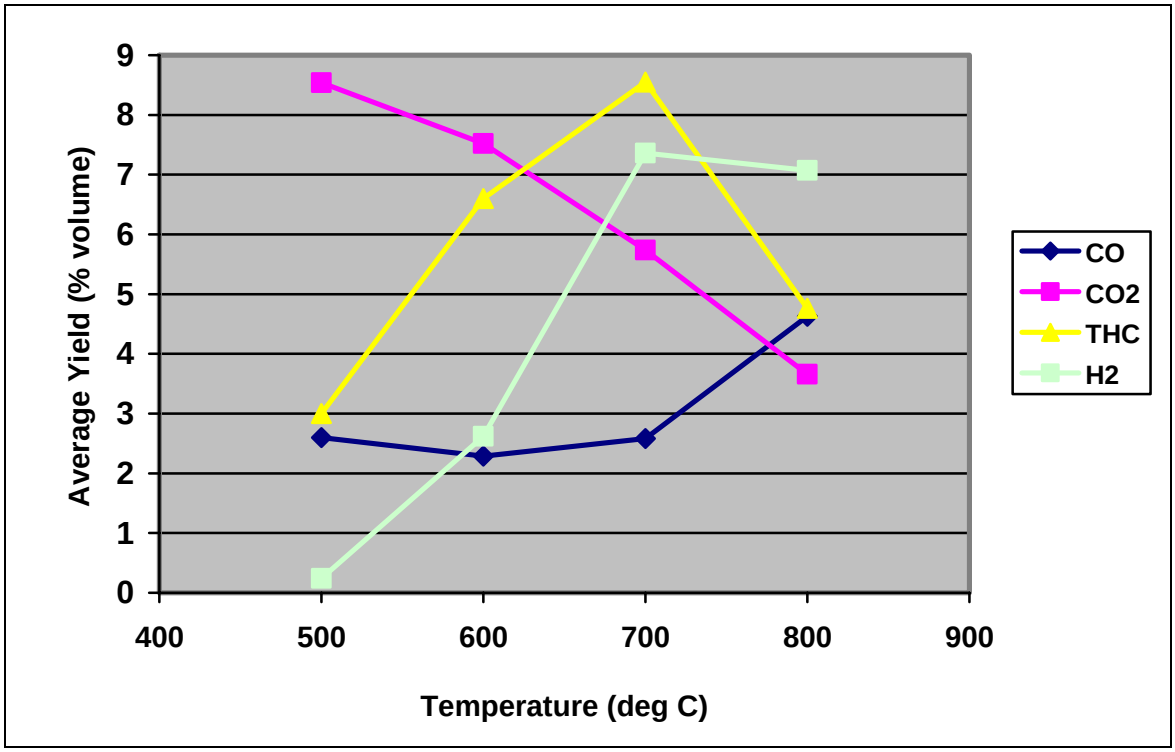


Figure 12. Average production of synthesis gas as affected by temperature.

4.3.4. *Liquid (Bio-Oil) Analysis*

The liquid product (bio-oil) was composed of the collected condensable gases (including moisture), tar and some solid products like ash and char that were carried through by the moving gases.

The liquid was red-brown to dark brown in color with some black portion at the bottom which is believed to be tar and char. The bio-oil has a strong, irritable odor that is common to all pyrolysis liquid from biomass (Tsai et al., 2006B). The liquid fraction was measured by weight. Encinar et al. (2000) stated that the small amount of liquids that is lost due to condensation and that high gas flow is impossible to prevent and was supplemented by means of weight difference. Table 9 shows some of the properties of

the liquid product. The pH level increased significantly ($p$-value = 0.0012) as the pyrolysis temperature was increased. One possible reason for this could be that the amount of water present in the bio-oil increased as temperature is increased. The secondary tar degradation at high temperatures (800°C) could have lead to the production of more $H_2$, CO, and several light HC and it is also possible to have an increased $H_2O$ production (Putun et al., 1999; Zabaniotou et al., 2000; Tsai et al., 2006B). The high water content in the bio-oil could also be the reason why the heating values as shown in table 9 are considerably lower than most commercial oil and petroleum products. There could also be high amounts of non-hydrocarbons present in the bio-oil such as $O_2$-rich compounds and ash. The bio-oils are commonly made of polar and non-polar organic components such as methanol, acetic acid, furfurals, and phenols. These organic components that are highly oxygenated are chemically bound with water and would need to be separated first and upgraded using either hydrocracking-hydrotreating or catalysis (i.e., zeolite synthesis) to increase the heating value and reduce corrosiveness when used as alternate fuel (Bridgewater and Grassi, 1991; Tsai et al., 2006B).

Table 9. Some properties of the liquid product.

| Temperature (°C) | $\rho_{ave}$ [a] (g cm$^{-3}$) | Average pH | HV (MJ kg$^{-1}$) |
|---|---|---|---|
| 500 | 0.982 | 4.7 | 2.430 |
| 600 | 0.992 | 5.7 | 2.336 |
| 700 | 1.015 | 6.6 | 2.011 |
| 800 | 1.009 | 7.6 | 2.020 |

[a] $\rho_{ave}$ = average density (including water and tar).

4.3.5. *Energy and Mass Balance*

Table 10 shows a simple energy balance for the modified batch pyrolysis experiment at each pyrolysis temperature. The parameters used for estimating energy balance were based on the calculated average product yield under the assumption that product losses were negligible. It was observed that the largest fraction of energy was contained in the char (70–83%) and followed by the gas (10–20%), while bio-oil has the least energy content (7–9%) (refer to table 11). The heating value of char was expected to be high because char has relatively high product yield and contained mostly organic carbon that could be similar to coal. The gaseous product was expected to have high heating value because it is mainly composed of highly combustible gases (i.e., CO, $H_2$, and low–molecular weight HC) or compounds released from the rapid devolatilization of cellulose, hemicellulose, and lignin. In addition, it was determined that the heating value of the gas from CGT pyrolysis (see table 10) is almost the same as the heating value of the gas from CGT gasification (3 to 8 MJ $m^{-3}$) between 704 and 871°C using 1 to 4 kg $m^{-3}$ solid fuel-to-air ratio (Hiler and Stout, 1985). The bio-oil, as stated earlier, has the least energy content because it has a high amount of chemically bound moisture and non-hydrocarbon compounds. Liquid upgrading through hydrotreating or catalytic cracking could significantly improve the quality of bio-oil.

Figure 13 shows a typical mass balance for the modified CGT pyrolysis at 500, 600, 700, and 800°C. The solid (char) production was favored greatly at lower temperatures while gas production was favored at higher temperatures.

Table 10. The heating values of each pyrolytic product from CGT at different pyrolysis temperatures.

| Temperature (°C) | HHV (MJ $kg^{-1}$) | | | Total HHV (MJ $kg^{-1}$) | Gas HHV (MJ $m^{-3}$) |
|---|---|---|---|---|---|
| | Char | Liquid | Gas | | |
| 500 | 19.23 | 2.43 | 2.74 | 24.40 | 3.37 |
| 600 | 20.33 | 2.34 | 5.28 | 27.94 | 6.41 |
| 700 | 21.64 | 2.01 | 6.78 | 30.43 | 7.73 |
| 800 | 19.70 | 2.02 | 4.26 | 25.98 | 4.71 |

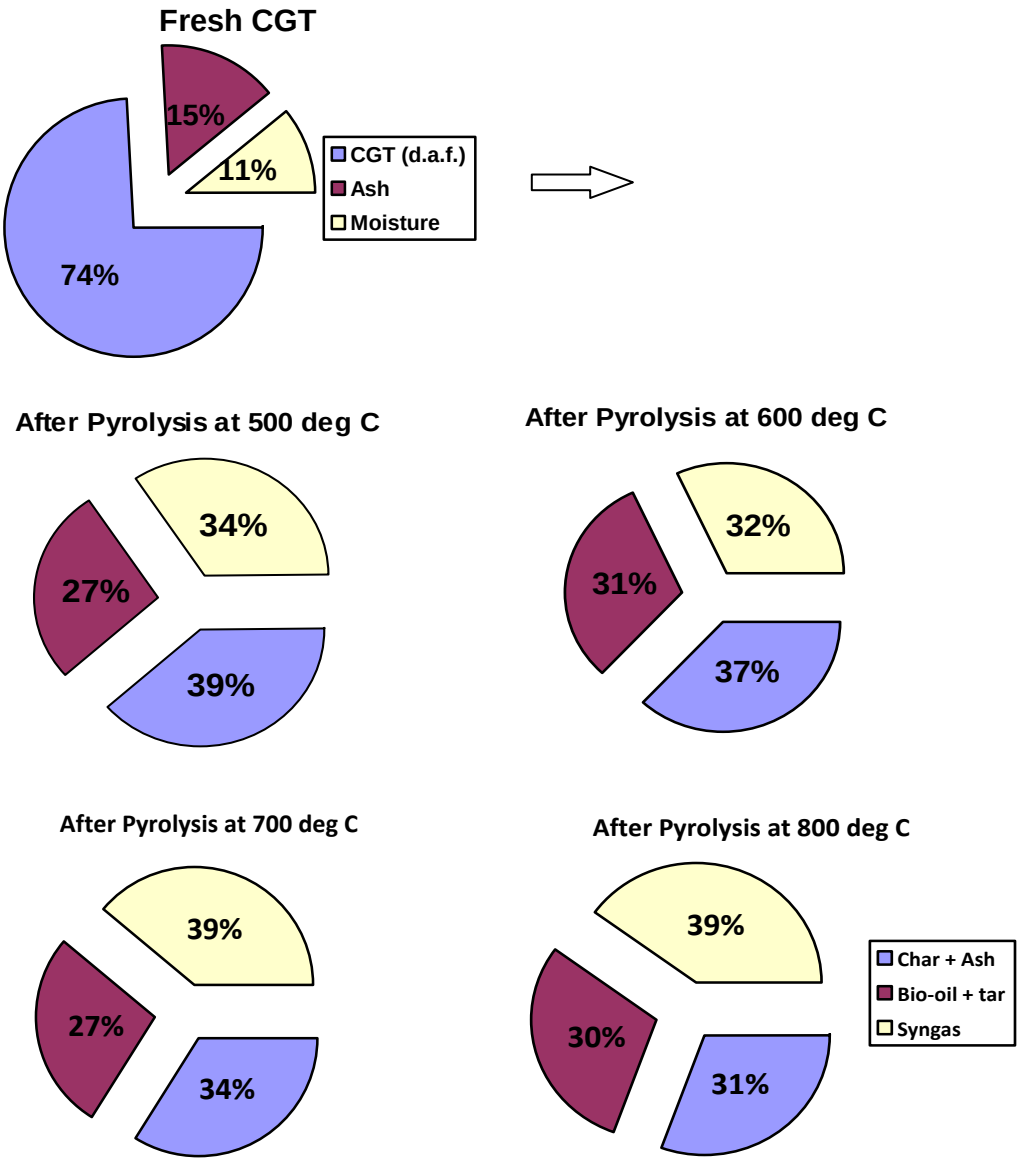


Figure 13. Typical mass balance for CGT pyrolysis at different temperatures.

Although CGT was utilized for energy production through batch pyrolysis and yielded a variety of energy products (i.e., char, bio-oil, and ash), the process was still considered energy intensive (Figure 14). The estimated energy required to pyrolyze 50 g of CGT was 6097 kJ, about 12 to 15 times higher than the total energy of the output products for all the temperature settings. The amount of energy used during the batch pyrolysis alone constituted more than 85% of the total energy input; the feedstock was around 13% while the remaining 3% was used for material preparation. The total energy output was only 7% to 10% of the total energy input which may indicate a very large energy loss (up to 97%) in the system (Figure 14). However, there are several factors that could have influenced the outcome of the pyrolysis process. The biomass used in the modified tests was only 20% (50 g) of the maximum capacity (250 g) of the pyrolyzer. The energy needed to pyrolyze the maximum amount of biomass using the same pyrolysis setup is the same as the energy used for 50 g CGT while a higher energy output is expected. Moreover, because batch pyrolysis was used, the energy input was expected to be high and may not necessarily be proportional to the amount of CGT being pyrolyzed. Therefore, there would be an excess energy that could contribute greatly to losses. The energy used during sample preparation could also be eliminated because the process used was batch pyrolysis and may be applied without further reducing the size of the material. Although it is claimed that particle size can have a major influence on the process rate of pyrolysis, Encinar et al. (2000) observed that particle size (e.g., *Cynara cardunculus* L.) had no influence on the main parameters such as temperature gradient inside the particles, which was also consistent with works using other residues (i.e., olive

and grape bagasse, maize, sunflower, grapevine, and tobacco) and could also be true for CGT. Therefore, if the energy used for sample preparation and pyrolysis will not be considered, the initial energy of the biomass would be relatively closer to the total energy of the output products. Energy losses would be in the range of 250–350 kJ or 30% to 46% of the original energy input which is still considerably high while the energy of the output represent between 55-70% of the input energy from CGT.

Table 11. A summary of the estimated energy input and output for CGT pyrolysis.

A. Input

| Process/Material | Energy (*kJ*) |
|---|---|
| 1) Preparation, $E_G$ | 139 |
| 2) Pyrolysis, $E_P$ | 5184 |
| 3) Biomass, $E_B$ | 774 |
| TOTAL | **6097** |

B. Output

| Temperature (°C) | Energy (*kJ*) | | | *E* output (*kJ*) |
|---|---|---|---|---|
| | Char | Liquid | Gas | |
| 500 | 367.84 | 33.27 | 47.11 | **448** |
| 600 | 370.60 | 40.04 | 77.59 | **488** |
| 700 | 365.74 | 27.60 | 131.43 | **525** |
| 800 | 300.75 | 29.84 | 85.10 | **416** |

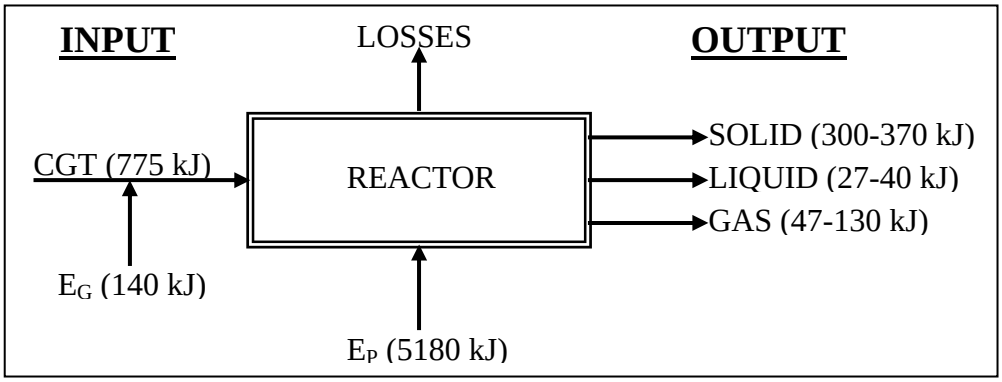


Figure 14. Typical energy balance for the modified pyrolysis process of CGT.

# 5. SUMMARY AND CONCLUSIONS

Pyrolysis of cotton-gin trash under different temperatures and reaction time settings have produced different amounts of pyrolytic products, i.e., in solid, liquid, and gaseous forms. In general, as the pyrolysis temperature increases, the char or solid production decreases and vice versa. In the first set of tests, the maximum solid yield after pyrolysis was about 40 wt.% at the pyrolysis temperature of 600°C and pyrolysis period of 30 min, but the heating value of the char was determined to be near the heating value of the unpyrolyzed CGT. In the modified pyrolysis experiment, the maximum char yield of about 38 wt.% was determined at 500°C while the lowest char yield of about 35 wt.% was determined at 800°C, both at the 30-min reaction time. The maximum char yields of the initial and modified tests were consistent having only approximately 2 wt.% difference but the pyrolysis temperature at which the maximum char yields were determined are not the same. The amount of CGT used in the initial test (ca. 100 g) was twice the amount of CGT used in the modified version (ca. 50 g). The pyrolysis temperature required to completely pyrolyze CGT into char at a fixed reaction time will depend on the amount of biomass. After proximate analysis of the char, an increase in the ash and fixed carbon percentages was observed as the temperature was increased while there was a decrease in volatile matter. The quality of char improved at higher temperature. It was also determined in the energy analysis that the heating value of char increased with increased temperature and comprises 70% to 83% of the total energy output in the modified test.

More gaseous products were generated at a higher temperature and longer pyrolysis time due to the rapid devolatilization and decomposition of biomass and char. The highest gaseous product yields (ca. 45 wt.%) were observed when the pyrolyzer was operated at higher temperatures (800°C) similar to that described in the literature, while the least gas yields were observed at lower temperatures (600°C). The gas produced was determined to be highly combustible, which could be due to the presence of producer or synthesis gas (CO, $H_2$, and THC). In the modified pyrolysis, the highest gaseous product yield of about 35 wt.% was determined at 800°C and the lowest (32 wt.%) was observed at 600°C. The gas yield trend was also consistent with the initial test result and with the literature. Nonetheless, the major composition of the gaseous product (CO, $CO_2$, THC, and $H_2$) in the modified test was determined using an on-line gas analyzer equipped with NDIR and TC detectors while THC was analyzed using a gas chromatograph with FID. The concentrations of CO, THC, and $H_2$ in the gas generally increased as the temperature was increased from 500 to 800°C but $CO_2$ showed otherwise. The concentration of $CO_2$ has decreased by almost 60% (mol) from 500 to 800°C. Meanwhile, the major composition of the hydrocarbons ($C_1$ to $C_6$) was determined. Methane ($C_1$), ethane ($C_2$), and propane ($C_3$) generally dominated the HC although pentane ($C_5$) showed unusually high amounts at 600 and 700°C. Methane has the highest percent volume in all pyrolysis runs and composed almost 50% of the THC at 800°C. The high fraction of flammable gases (CO, $H_2$, and THC) in the gaseous product has contributed to its energy content that was 10–20% of the total energy output.

The amount of liquid (bio-oil) produced from the initial tests was lower compared to the char and gas production. The liquid bio-oil produced contained appreciable amounts of water as verified by its density. Although small amounts of liquids were produced, an obvious trend was still established from the results. As the temperature increases, the liquid production increases; on the other hand, there was an inverse relationship between the liquid and the pyrolysis time. This result was slightly different compared to the modified pyrolysis test. The yield of bio-oil increased significantly from 500 to 600°C but decreased slightly from 600 to 800°C. The production of bio-oil is greatly favored by rapid heating at lower pyrolysis temperatures (400–500°C) and shorter residence time. The conventional pyrolysis mode used in both experiments gave higher char yield and lower bio-oil yield. The energy content of bio-oil in the modified test was determined to be very low (2–3 MJ $kg^{-1}$) because it was highly oxygenated and contains large portion of chemically bound water and non-HC compounds.

The entire pyrolysis process was considered an energy-intensive process due to the high amount of energy input which was estimated at around 6100 kJ. The total energy output from the different products constituted only 7% to 10% of the energy input. Several factors may have affected the inconsistency in process (i.e., amount of biomass and sample preparation); however, after disregarding the energy used for preparation and pyrolysis, the energy losses still ranged from 30% to 46 % while the energy of the output represent between 55-70% of the input energy from CGT.

# 6. RECOMMENDATIONS FOR FUTURE RESEARCH

The aim of this research was primarily for the determination and quantification of the different products of CGT pyrolysis. The preliminary characterization of each product was also initiated but still needs a thorough analysis to identify the components or unique properties that could be further utilized for energy production. There are many factors that could influence the product yield from pyrolysis. Some of the major factors include temperature, residence or reaction time, heating rate, particle size distribution (PSD), sweep gas flowrate, and pressure. Due to time, equipment, and material constraints, only the effect of temperature and reaction time were observed in this study. Nonetheless, some studies showed significant variation in product yield using different heating rates. Slow pyrolysis or carbonization that could last from hours to days produces more char at pressure between 0.01 and 1 bar while fast pyrolysis favors bio-oil production at around 1.0 bar. Meanwhile, it is generally expected that particle size would affect the temperature gradients inside the particle which could possibly increase solid yields and decrease gas and liquid yields. The sweep-gas flow rate affects the residence time of the vapor phase from pyrolysis and thus minimizes secondary product degradation. All these factors still need to be further optimized to favor solid, liquid, or gaseous production from cotton-gin trash pyrolysis.

The process used for this study falls under the conventional pyrolysis category which primarily produces a considerable portion of all pyrolytic products (solid, liquid, and gaseous). Here, we characterized the solid product by proximate analysis and

heating value; the liquid product by acidity, density, and heating value; and the gaseous product by gas analysis and chromatography. The char having a high heating value can be used directly in a coal-fired generator to produce electricity. Char activation is also an option for use in waste water treatment and water purification system. Odor emission control is also a promising area of application for activated char but porosity and affinity to odorous compounds should be further studied. The bio-oil from CGT still needs to be analyzed by gas chromatograph/mass spectrometer (GC/MS) to scan for potential and abundant high-value compounds present. When this is done, products upgrading by using either hydro-treating–hydrocracking or catalytic conversion (zeolite) should be the next step. Some studies found that bio-oil can be used as a direct substitute for petroleum oil due to their compatibility. The bio-oil and char slurry are also reported as potential alternate fuels for large engines but still need more research to verify their efficiency. The synthesis gas (syngas) was determined to be composed mainly of CO, $H_2$, and other lightweight HC. Due to the high fraction of flammable gases, syngas could be readily burned and used to power a steam generator or even the pyrolyzer itself. The gas could also be catalyzed and reformed to produce high-value chemicals for different energy applications.

In summary, the following items need to be considered in future research for CGT pyrolysis:

1) Continuous improvement of the design of the pyrolyzer or fabrication of a continuously fed pyrolysis system

2) Optimize pyrolysis parameters such as heating rate, particle size, sweep-gas flowrate, and pressure;
3) Complete elemental analysis for CGT, char, and bio-oil to conduct an accurate mass and energy balance;
4) Complete bio-oil compound characterization using GC/MS;
5) Products upgrading (liquid and gas) by hydrotreating or catalytic cracking; and
6) Complete economic analysis to justify large-scale production.

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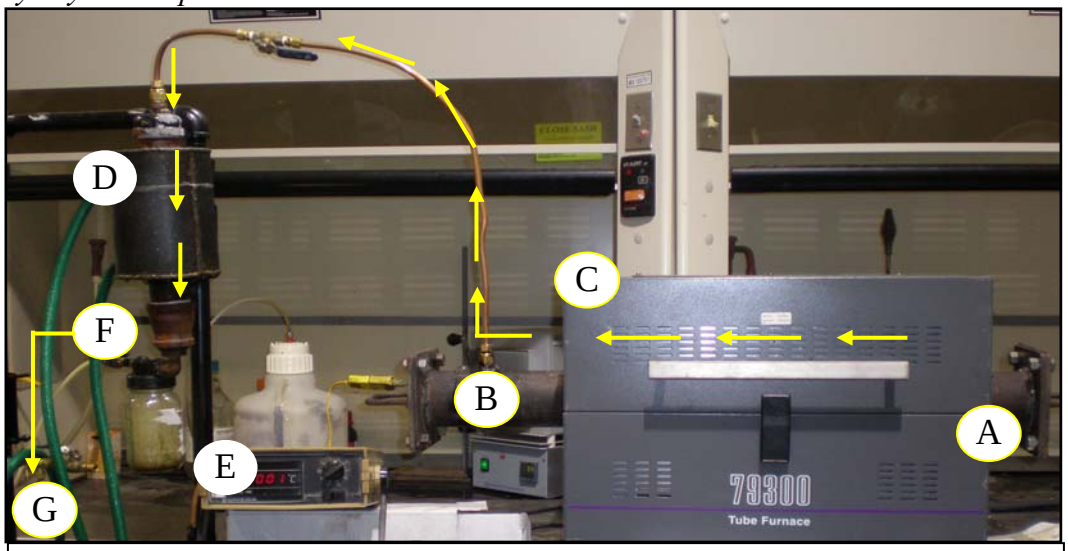
# APPENDIX A

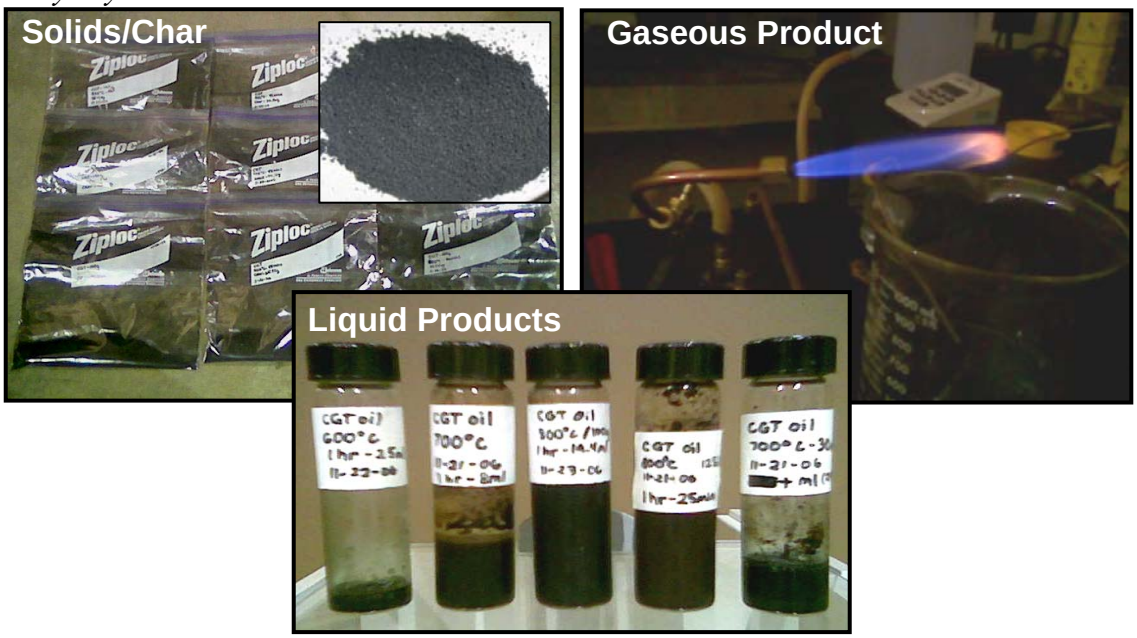
Photos from the Experiment

*A. Pyrolysis Setup*




**Preliminary pyrolysis setup**: (A) steel container, (B) horizontal tube reactor, (C) programmable tube furnace, (D) condenser, (E) thermocouple reader, (F) liquid collector/cold trap, and (G) volume displacement tanks.

*B.Pyrolytic Products*



# APPENDIX B

Equations and Assumptions Used in the Analysis of Results

1. Approximation of High Heating Value of Biomass using Proximate Analysis:

A) Parikh et al., 2004:

$$HHV\,(MJ \cdot kg^{-1}) = 0.3536(FC) + 0.1559(VM) + 0.0078(ASH)$$

B) Demirbas, 1997:

$$HHV\,(MJ \cdot kg^{-1}) = 0.312(FC) + 0.1534(VM) \qquad \text{(a)}$$

$$HHV\,(MJ \cdot kg^{-1}) = 0.196(FC) + 14.119 \qquad \text{(b)}$$

2. Average Yield of Pyrolytic Products:

A) $\%\,\text{Solid (char)} = \left(\dfrac{\text{Char wt.}}{\text{Total wt.}}\right) \times 100\%$

B) $\%\,\text{Liquid (Bio-oil)} = \left(\dfrac{\text{Liquid wt.}}{\text{Total wt.}}\right) \times 100\%$

C) $\%\,\text{Gas Yield} = 100\% - \%\,\text{Solid (char)} - \%\,\text{Liquid (Bio-oil)}$

Assuming no losses (Losses ~ 0)

3. Molecular Wt. (MW in g $mol^{-1}$) of Gas at standard temperature and pressure (STP):

STP (defined by the US Environmental Protection Agency, EPA):

T = 25 °C + 273.15 K

P = 1 atm = 101.325 kPa

R = 0.0826 L-atm $(g\text{-}mol\text{-}K)^{-1}$

A) Average MW (g $mol^{-1}$) of the gaseous product:

1. $MW_{ave}\ (g\text{-}mol^{-1}) = \sum \left(MW_i \times (\%\ Conc)_i\right)$

$$MW_{ave}\ (g\text{-}mol^{-1}) = MW_{CO}\,(\%\ CO) + MW_{CO2}\,(\%\ CO_2) + MW_{THC}\,(\%\ THC) + MW_{O2}\,(\%\ O_2) + MW_{H2}\,(\%\ H_2) + MW_{N2}\,(\%\ N_2)$$

2. $MW_{THC}\ (g\text{-}mol^{-1}) = \sum \left(HC_i \times (mole\ \%)_i\right)$

$$MW_{ave}\ (g\text{-}mol^{-1}) = MW_{C1}\,(\%\ C_1) + MW_{C2}\,(\%\ C_2) + MW_{C3}\,(\%\ C_3) + MW_{C4}\,(\%\ C_4) + MW_{C5}\,(\%\ C_5) + MW_{C6}\,(\%\ C_6) + MW_{Others}\,(\%\ Others)$$

3. $MW_{Others}\,(g\text{-}mol^{-1}) = \left(\frac{MW_{C4} + MW_{C5}}{2}\right)$

Assuming most of the unidentified HC are between $C_4$ and $C_5$.

B) Total Gas Volume, $V_G$ ($m^3$) at STP:

$$V_G\ (m^3) = \left(\frac{M_{ave}}{\rho}\right)$$

Average mass, $M_{ave}$ (g) = known (by difference)

Density, $\rho$ (g $m^{-3}$) = ($MW_{ave}$) x $\left(\frac{n}{V}\right)$

Using ideal gas equation: $\left(\frac{n}{V}\right) = \frac{P}{RT}$ (mol $m^{-3}$)

# APPENDIX C

Statistical Analysis (SPSS)

1. *Pyrolytic Products*

**Multiple Comparisons**

Dependent Variable: Solid
Bonferroni

| (I) varSolid | (J) varSolid | Mean Difference (I-J) | Std. Error | Sig. | 95% Confidence Interval | |
|---|---|---|---|---|---|---|
| | | | | | Lower Bound | Upper Bound |
| 500 | 600 | 1.95667 | .84719 | .325 | -1.1236 | 5.0369 |
| | 700 | 4.58333* | .84719 | .006 | 1.5031 | 7.6636 |
| | 800 | 7.85667* | .84719 | .000 | 4.7764 | 10.9369 |
| 600 | 500 | -1.95667 | .84719 | .325 | -5.0369 | 1.1236 |
| | 700 | 2.62667 | .75775 | .063 | -.1284 | 5.3817 |
| | 800 | 5.90000* | .75775 | .001 | 3.1450 | 8.6550 |
| 700 | 500 | -4.58333* | .84719 | .006 | -7.6636 | -1.5031 |
| | 600 | -2.62667 | .75775 | .063 | -5.3817 | .1284 |
| | 800 | 3.27333* | .75775 | .021 | .5183 | 6.0284 |
| 800 | 500 | -7.85667* | .84719 | .000 | -10.9369 | -4.7764 |
| | 600 | -5.90000* | .75775 | .001 | -8.6550 | -3.1450 |
| | 700 | -3.27333* | .75775 | .021 | -6.0284 | -.5183 |

*. The mean difference is significant at the .05 level.

**Multiple Comparisons**

Dependent Variable: Liquid
Bonferroni

| (I) varLiquid | (J) varLiquid | Mean Difference (I-J) | Std. Error | Sig. | 95% Confidence Interval | |
|---|---|---|---|---|---|---|
| | | | | | Lower Bound | Upper Bound |
| 500 | 600 | -7.17167* | 1.73066 | .026 | -13.4640 | -.8793 |
| | 700 | -.37833 | 1.73066 | 1.000 | -6.6707 | 5.9140 |
| | 800 | -2.45833 | 1.73066 | 1.000 | -8.7507 | 3.8340 |
| 600 | 500 | 7.17167* | 1.73066 | .026 | .8793 | 13.4640 |
| | 700 | 6.79333* | 1.54795 | .019 | 1.1653 | 12.4214 |
| | 800 | 4.71333 | 1.54795 | .112 | -.9147 | 10.3414 |
| 700 | 500 | .37833 | 1.73066 | 1.000 | -5.9140 | 6.6707 |
| | 600 | -6.79333* | 1.54795 | .019 | -12.4214 | -1.1653 |
| | 800 | -2.08000 | 1.54795 | 1.000 | -7.7080 | 3.5480 |
| 800 | 500 | 2.45833 | 1.73066 | 1.000 | -3.8340 | 8.7507 |
| | 600 | -4.71333 | 1.54795 | .112 | -10.3414 | .9147 |
| | 700 | 2.08000 | 1.54795 | 1.000 | -3.5480 | 7.7080 |

*. The mean difference is significant at the .05 level.

**Multiple Comparisons**

Dependent Variable: Gas
Bonferroni

| (I) varGas | (J) varGas | Mean Difference (I-J) | Std. Error | Sig. | 95% Confidence Interval | |
|---|---|---|---|---|---|---|
| | | | | | Lower Bound | Upper Bound |
| 500 | 600 | 5.22000 | 2.25756 | .324 | -2.9880 | 13.4280 |
| | 700 | -4.20000 | 2.25756 | .631 | -12.4080 | 4.0080 |
| | 800 | -5.39333 | 2.25756 | .289 | -13.6014 | 2.8147 |
| 600 | 500 | -5.22000 | 2.25756 | .324 | -13.4280 | 2.9880 |
| | 700 | -9.42000* | 2.01922 | .014 | -16.7615 | -2.0785 |
| | 800 | -10.61333* | 2.01922 | .007 | -17.9548 | -3.2718 |
| 700 | 500 | 4.20000 | 2.25756 | .631 | -4.0080 | 12.4080 |
| | 600 | 9.42000* | 2.01922 | .014 | 2.0785 | 16.7615 |
| | 800 | -1.19333 | 2.01922 | 1.000 | -8.5348 | 6.1482 |
| 800 | 500 | 5.39333 | 2.25756 | .289 | -2.8147 | 13.6014 |
| | 600 | 10.61333* | 2.01922 | .007 | 3.2718 | 17.9548 |
| | 700 | 1.19333 | 2.01922 | 1.000 | -6.1482 | 8.5348 |

*. The mean difference is significant at the .05 level.

2. *Properties of Char*

**Multiple Comparisons**

Dependent Variable: ASH
Bonferroni

| (I) varASH | (J) varASH | Mean Difference (I-J) | Std. Error | Sig. | 95% Confidence Interval | |
|---|---|---|---|---|---|---|
| | | | | | Lower Bound | Upper Bound |
| 500 | 600 | -5.76000* | 1.38603 | .019 | -10.5818 | -.9382 |
| | 700 | -7.54000* | 1.38603 | .004 | -12.3618 | -2.7182 |
| | 800 | -8.84000* | 1.38603 | .001 | -13.6618 | -4.0182 |
| 600 | 500 | 5.76000* | 1.38603 | .019 | .9382 | 10.5818 |
| | 700 | -1.78000 | 1.38603 | 1.000 | -6.6018 | 3.0418 |
| | 800 | -3.08000 | 1.38603 | .342 | -7.9018 | 1.7418 |
| 700 | 500 | 7.54000* | 1.38603 | .004 | 2.7182 | 12.3618 |
| | 600 | 1.78000 | 1.38603 | 1.000 | -3.0418 | 6.6018 |
| | 800 | -1.30000 | 1.38603 | 1.000 | -6.1218 | 3.5218 |
| 800 | 500 | 8.84000* | 1.38603 | .001 | 4.0182 | 13.6618 |
| | 600 | 3.08000 | 1.38603 | .342 | -1.7418 | 7.9018 |
| | 700 | 1.30000 | 1.38603 | 1.000 | -3.5218 | 6.1218 |

*. The mean difference is significant at the .05 level.

**Multiple Comparisons**

Dependent Variable: FC
Bonferroni

| (I) varFC | (J) varFC | Mean Difference (I-J) | Std. Error | Sig. | 95% Confidence Interval | |
|---|---|---|---|---|---|---|
| | | | | | Lower Bound | Upper Bound |
| 500 | 600 | 2.88333 | 2.53532 | 1.000 | -5.9367 | 11.7034 |
| | 700 | -4.79300 | 2.53532 | .572 | -13.6131 | 4.0271 |
| | 800 | -8.45033 | 2.53532 | .062 | -17.2704 | .3697 |
| 600 | 500 | -2.88333 | 2.53532 | 1.000 | -11.7034 | 5.9367 |
| | 700 | -7.67633 | 2.53532 | .098 | -16.4964 | 1.1437 |
| | 800 | -11.33367* | 2.53532 | .012 | -20.1537 | -2.5136 |
| 700 | 500 | 4.79300 | 2.53532 | .572 | -4.0271 | 13.6131 |
| | 600 | 7.67633 | 2.53532 | .098 | -1.1437 | 16.4964 |
| | 800 | -3.65733 | 2.53532 | 1.000 | -12.4774 | 5.1627 |
| 800 | 500 | 8.45033 | 2.53532 | .062 | -.3697 | 17.2704 |
| | 600 | 11.33367* | 2.53532 | .012 | 2.5136 | 20.1537 |
| | 700 | 3.65733 | 2.53532 | 1.000 | -5.1627 | 12.4774 |

*. The mean difference is significant at the .05 level.

**Multiple Comparisons**

Dependent Variable: VM
Bonferroni

| (I) varVM | (J) varVM | Mean Difference (I-J) | Std. Error | Sig. | 95% Confidence Interval | |
|---|---|---|---|---|---|---|
| | | | | | Lower Bound | Upper Bound |
| 500.00 | 600.00 | 2.87800 | 1.71568 | .792 | -3.0906 | 8.8466 |
| | 700.00 | 12.33500* | 1.71568 | .001 | 6.3664 | 18.3036 |
| | 800.00 | 17.29233* | 1.71568 | .000 | 11.3237 | 23.2610 |
| 600.00 | 500.00 | -2.87800 | 1.71568 | .792 | -8.8466 | 3.0906 |
| | 700.00 | 9.45700* | 1.71568 | .003 | 3.4884 | 15.4256 |
| | 800.00 | 14.41433* | 1.71568 | .000 | 8.4457 | 20.3830 |
| 700.00 | 500.00 | -12.33500* | 1.71568 | .001 | -18.3036 | -6.3664 |
| | 600.00 | -9.45700* | 1.71568 | .003 | -15.4256 | -3.4884 |
| | 800.00 | 4.95733 | 1.71568 | .121 | -1.0113 | 10.9260 |
| 800.00 | 500.00 | -17.29233* | 1.71568 | .000 | -23.2610 | -11.3237 |
| | 600.00 | -14.41433* | 1.71568 | .000 | -20.3830 | -8.4457 |
| | 700.00 | -4.95733 | 1.71568 | .121 | -10.9260 | 1.0113 |

*. The mean difference is significant at the .05 level.

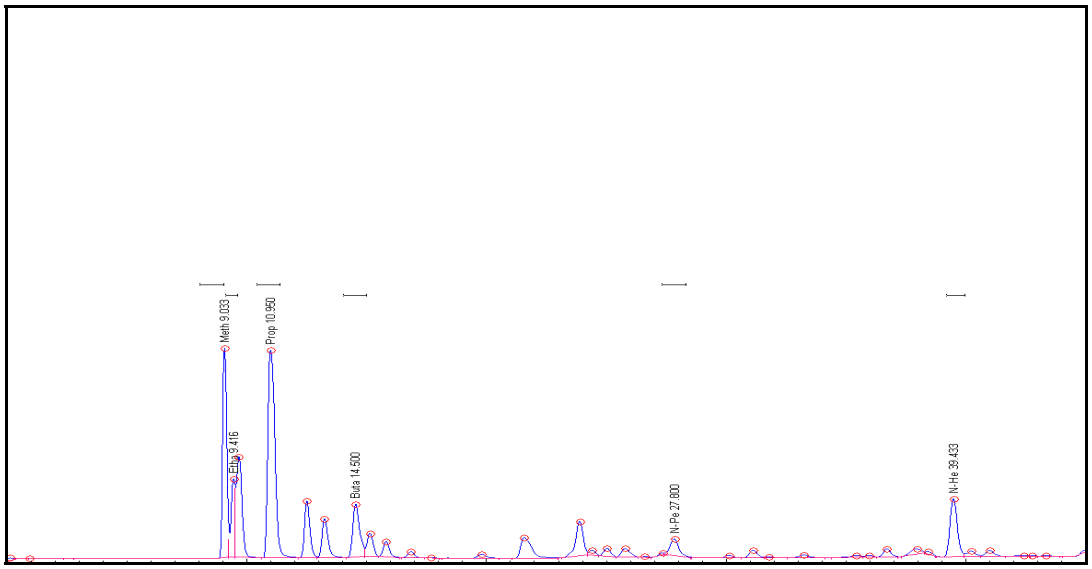
**Multiple Comparisons**

Dependent Variable: HV
Bonferroni

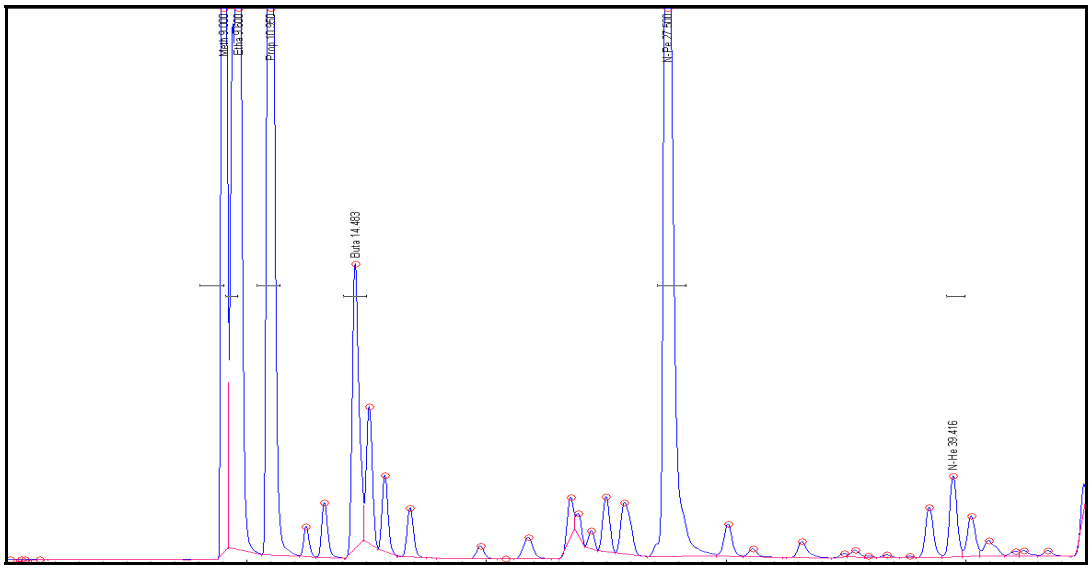
| (I) varHV | (J) varHV | Mean Difference (I-J) | Std. Error | Sig. | 95% Confidence Interval | |
|---|---|---|---|---|---|---|
| | | | | | Lower Bound | Upper Bound |
| 500 | 600 | -474.02667 | 513.41226 | 1.000 | -2260.1259 | 1312.0725 |
| | 700 | -1041.0700 | 513.41226 | .463 | -2827.1692 | 745.0292 |
| | 800 | -204.48000 | 513.41226 | 1.000 | -1990.5792 | 1581.6192 |
| 600 | 500 | 474.02667 | 513.41226 | 1.000 | -1312.0725 | 2260.1259 |
| | 700 | -567.04333 | 513.41226 | 1.000 | -2353.1425 | 1219.0559 |
| | 800 | 269.54667 | 513.41226 | 1.000 | -1516.5525 | 2055.6459 |
| 700 | 500 | 1041.07000 | 513.41226 | .463 | -745.0292 | 2827.1692 |
| | 600 | 567.04333 | 513.41226 | 1.000 | -1219.0559 | 2353.1425 |
| | 800 | 836.59000 | 513.41226 | .851 | -949.5092 | 2622.6892 |
| 800 | 500 | 204.48000 | 513.41226 | 1.000 | -1581.6192 | 1990.5792 |
| | 600 | -269.54667 | 513.41226 | 1.000 | -2055.6459 | 1516.5525 |
| | 700 | -836.59000 | 513.41226 | .851 | -2622.6892 | 949.5092 |

## APPENDIX D

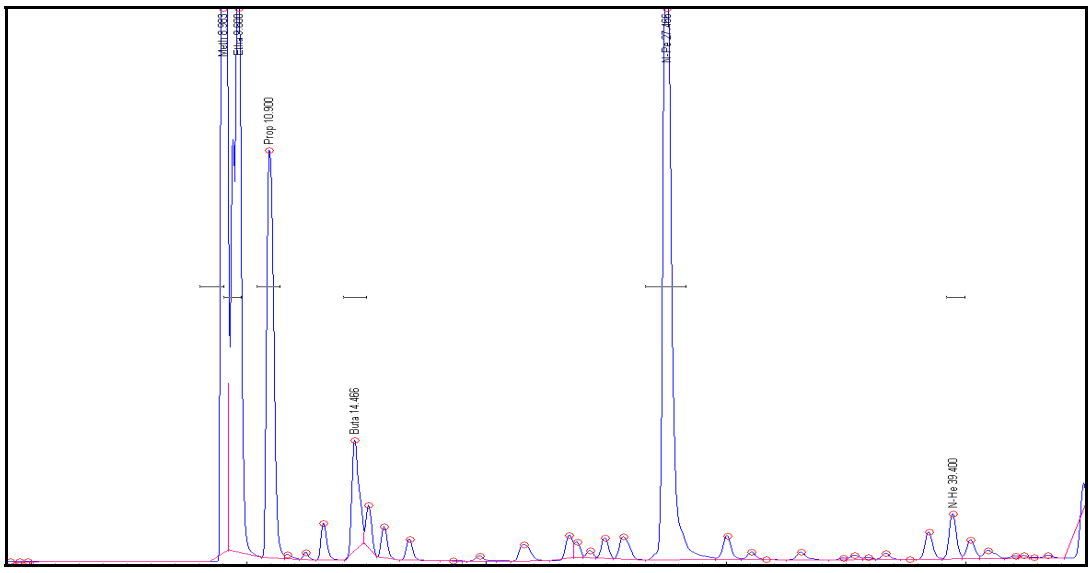
Sample gas chromatograms of the THC in the gaseous products.



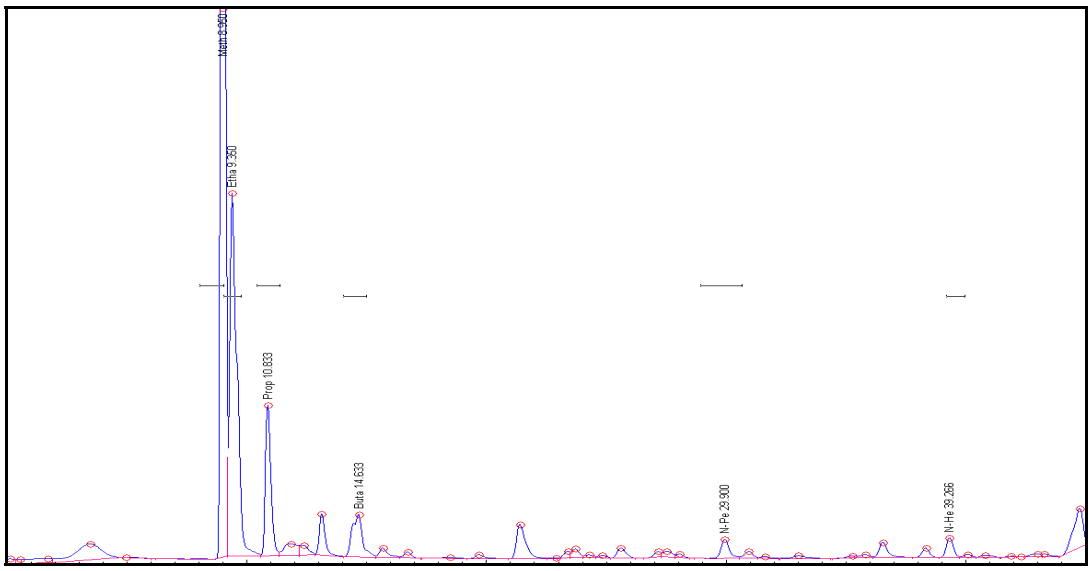

A. GC-FID for gas at 500 °C, 25µL, 0-1000, 0-45min.




B. GC-FID for gas at 600 °C, 25µL, 0-1000, 0-45min.




C. GC-FID for gas at 700 °C, 25µL, 0-1000, 0-45min.




D. GC-FID for gas at 800 °C, 25µL, 0-1000, 0-45min.

# VITA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- 2007 ASABE Centennial Annual International Meeting, Minneapolis, MN.
- 2007 Beltwide Cotton Conference, New Orleans, LA, January 8–11, 2007. (2nd Place – Student Paper Competition). Paper No. 6706. (F.L. Aquino, S.C. Capareda, J.R. Hernandez, and J. Powell)